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The separation of the rare earths by ion exchange

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THE SEPARATION OF THE RARE EARTHS BY ION EXCHANGE

by

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INTRODUCTION

I Preliminary Remarks

The elements possessing the atomic numbers 58-71 inclusive make up the group of elements known as the rare earths. The principal valence of the group is three, and the chemical reactions of each element in the trivalent state are the same. If differences should exist, they are differences of degree, and not of kind. Because of the fact that yttrium and scandium are very similar to the rare earths chemically, these two elements are generally included in the discussion.

The isolation of one rare earth species from the others represents one of the most difficult separations to be found anywhere in the field of inorganic chemistry. Until the present time, many prominent chemists have devoted years, even lifetimes, to isolating and purifying small amounts of salts of the individual rare earths. It is only natural, then, that these scientists were very reluctant to either sell or loan many of the rare earth salts for fear of losing them or fear of loss through contamination.

At the present time, there are only a few commercial uses for any of the rare earths. Lanthanum is used in some optical glass, and cerium is used in gas mantles and also as

a chemical reagent. Such a state of affairs can no doubt be attributed to the inaccessibility of these compounds to the scientific world. It is hoped that the method to be outlined forthwith will be adopted or improved by other investigators so that a sufficient amount of the individual rare earths can be made available to chemists in general at a reasonable price so that industrial applications can be investigated and, perhaps, exploited.

The separations process to be described employs the use of an artificial ion-exchange resin, and is an outgrowth of the tremendous amount of research performed during the war years by numerous men connected with the Manhattan Project. The problem was first suggested to the author by Dr. F. H. Spedding during January, 1945. Equipment was assembled as quickly as possible, and the first experimental results were reported the following month. By October 1, 1945, the experimental results reported herein had been obtained, with the exception of those listed in Tables 15, 16, and 17. The experimental work was performed by the author with valuable assistance from Mr. N. R. Sleight and Mr. J. M. Wright. Dr. A. F. Voigt aided materially with his many helpful suggestions. The work of this small group was under the able direction of Dr. F. H. Spedding. Mention of this is made here because the author feels that more credit is due these gentlemen than could be expressed in a mere acknowledgment.

II Review of the Literature

a) The chemical and physical behavior of the rare earths. Probably no other group of elements has chemical properties which are so similar within themselves as are the elements in Group III-A of the periodic system. This group consists of yttrium, scandium, the rare earths, and actinium. Scandium and yttrium are called "rare earth-like" elements because their chemical properties and many physical properties are similar to the true rare earths. Yttrium, in particular, clings tenaciously to the rare earths in any separation scheme. Actinium does not occur in any great amount in nature since it exists only as an intermediate element in a radioactive decay chain. Therefore, not much effort has been expended in developing specific reactions of this element. Scandium can be separated from the other members of this group with relative ease by taking advantage of the slight solubility of the complex it forms with NH_4HF_2.

The ions of the elements in Group III-A are normally trivalent. It is in the trivalent state that the chemistry of all these elements is so similar. The reaction chemistry of the rare earths is surveyed in detail by Vickery (1), (2) and by Mellor (3). Particular emphasis in these references is placed upon the methods of separation, identification, and determination of the individual rare earths.

Valence states other than the trivalent state are known for some of the rare earths. Cerium, and possibly terbium have a stable tetravalent state, while europium, ytterbium, and samarium exhibit bivalent ions in solution. Good use can be made of these valence states to effect some sort of a separation of these particular elements from the bulk of rare earths which are only trivalent.

The reasons for the chemical similarity between the members of the rare earth group can be explained from the standpoint of the electronic configurations of the ions. The outermost shells of the trivalent rare earth ions which contain electrons are the 4f, 5s, and 5p shells. The latter two (5s and 5p) are complete within themselves and tend to shield the 4f shell from any external fields. The rare earths differ from each other in the number of electrons within the 4f shell. Since the 4f shell contains seven orbitals, the existence of fourteen members in the group is explained. The electrons in the 4f shell do not lend themselves to the formation of chemical bonds with other atoms because of the shielding effect of the 5s and 5p shells. Hence, the 4f electrons are perturbed very slightly by external fields from neighboring ions, atoms, or dipoles. It follows directly that these elements should be similar chemically since they differ from each other only by the charge on the nucleus and the number of electrons in the 4f shell.

The configuration of the rare earth ions accounts for a large number of their physical properties and characteristics. Of especial importance to this work are the absorption spectra of the ions which have been shown to result from transitions of the electrons between states within the 4f shell. These are "forbidden" transitions since there is no change in the value of the azimuthal quantum numbers of the individual electrons as is necessary for ordinary dipole radiation. Forbidden transitions are not very intense, being $\sim 10^{-3}$ times that of the dipole radiation. What such transitions lack in intensity, they make up in the sharpness of the absorption bands. It is because of the sharpness of the absorption bands that spectral methods lend themselves so well as a tool for analysis of rare earth mixtures (4). A summary concerning the spectra of the rare earths has been published by Freed (5) and by Van Vleck (6).

The rare earths furnished a fertile field for the application of modern concepts regarding the paramagnetism of the ions. The theory that successfully explained the paramagnetism for the transition elements did not apply to the rare earths. With the transition elements, the S quantum number can be neglected, the paramagnetism being dependent only upon the value of L (7, 8). With the rare earths the inner quantum number J (the vector sum of L and S) must be employed because the 4f electrons are in a shielded shell,

and J remains a good quantum number. The differences in paramagnetism between the rare earth ions are so great that a method for the analysis of a mixture has been worked out along these lines (9).

Of particular interest to chemists is the "lanthanide" contraction which is the contraction of the ionic size of the rare earth ion as the atomic number is increased. The contraction is due to the greater nuclear charge and its influence on the outermost 5s and 5p shells as the inner 4f shell is being filled. The amount of ion-dipole attraction (or hydration of the ions in solution) is increased, with the result that the size of the hydrated ion becomes greater with an increase in atomic number. This is an important factor in the separation process to be described in the thesis, and it will be discussed further in a later section. The yttrium ion, with an atomic number of only 39, attracts such a large number of water dipoles that it becomes comparable in size to the hydrated rare earth ions. It is because of this fact and the fact that yttrium is in Group III-A that it is similar to the rare earths in all of its chemical reactions. The effects of the lanthanide contraction do not stop with the rare earth group, but extend to hafnium and, to a lesser extent, tantalum. This serves to explain why the separations of hafnium from zirconium and tantalum from columbium are so difficult.

b) <u>The methods for separation</u>. Historically, the first

means of separating the rare earths from each other was through the use of repeated fractional crystallizations. This method is still in use today, the advances being made in the better choice of the conditions and the anions used in the crystallization process. A great number of fractionations were required to prepare pure salts, this number often exceeding one thousand (10). It is evident that the yield of pure product would be necessarily low. One of the foremost workers in the field of rare earth chemistry, Prandtl, has summarized his efforts in a comprehensive article (11) in which he proposes numerous schemes for separating and purifying each of the rare earths. The fractional crystallizations must be carried out at constant temperature and at a slow rate. Various reagents are used in effecting the separation. Most noteworthy are the sulfate (12), the magnesium double nitrate (13), the bromate (14), and the basic nitrate (15). Numerous other reagents have been reported in the literature which are used at controlled pH values and which employ the principle of small differences in solubility as a direct consequence of small differences in the basicities of the various rare earth ion species.

Considerable use has been made of the anomalous valence states of Ce, Sm, Eu, and Yb for effecting separations from each other and from the remaining rare earths. Cerium, with its tetravalent state in solution, can be

separated quantitatively from the other rare earths quite easily. Europium and samarium possess divalent ions in solution because of the tendency of the ions to half fill the 4f shell with electrons; ytterbium exhibits the bivalent state because it tends to complete the 4f shell (Hunds rule). The bivalent state of these three elements is achieved quite readily by reducing the normal trivalent ions with a Jones reductor (16), electrolytically (17), or with a dilute sodium amalgam (18). Actual formation of the amalgams of Eu, Sm, and Yb has been achieved under controlled conditions (19). Some contamination occurs because of a slight tendency of other rare earths to undergo amalgam formation. Holleck (20) has reported that bivalent states of La, Ce, Pr, Nd, and Gd can be obtained under certain conditions, but they are very unstable and easily oxidized.

The rare earth group is often considered to consist of two sub-groups, the yttrium earths, and the cerium earths, although the line of demarcation is by no means sharp. The sub-groups were so named since cerium and yttrium are the principal rare earth constituents of the minerals which contain them. The cerium group consists of La, Ce, Pr, Nd, 61, Sm, and Eu while the yttrium group contains Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. A separation of one group from the other can be effected by using a double sulfate precipitation with K_2SO_4 or $(NH_4)_2SO_4$ (21,22,23). Other investigators favor

the use of Tl_2SO_4 (24). The yttrium earths are generally more soluble. There is considerable overlapping from one group to the other, principally with Sm, Eu, Gd, and Tb. Prandtl (11) considers a scheme which is useful in removing the bulk of these four elements from both the light and heavy ends of the rare earth group.

A liquid extraction process has been tried (25) which employs various organic solvents, but with not too much success. However, Appleton and Selwood (26) treated aqueous solutions of lanthanum and neodymium thiocyanates with n-butyl alcohol with the result that the Nd/La ratio in the alcohol layer to the Nd/La ratio in the aqueous layer was 1.06. It may be possible to prepare large amounts of these two elements in a pure state through use of an efficient liquid-liquid extractor.

The methods of chromatography have been applied to the separation of the rare earths. The chromatographic method employs the use of a column, packed with adsorbent. A solution of a mixture of materials is percolated through the packed column and a separation is effected through preferential surface adsorption. This method was first proposed for use with the rare earths by Lange and Nagel (27) in which they report that any separation obtained would be dependent upon the proper choice of adsorbent and of the solvent used as the eluent. The work of Botti (28) illustrated the use of activated carbon for the adsorption. The

method seemed to work best for Sm and Gd, but only slight enrichments were obtained. Frametsa (29, 30) used Al_2O_3 as the adsorbent, and eluted the material off the adsorbent using a solution of Rochelle salts. Results showed that the yttrium was adsorbed more strongly than the cerium group. The process was independent of the pH of the eluant. When citric acid was added to the eluant, the order of the adsorption series in the lanthanum group was reversed. The separation was not clean, but instead gave only a partial enrichment. In an attempt to separate trivalent cerium from trivalent lanthanum by adsorbing the ions on Al_2O_3, Croatto (31) was only able to show that Ce^{+++} was adsorbed more strongly.

The use of a high capacity ion exchange column was introduced by Russell and Pearce (32). The method of ion exchange differs from chromatography in that in the adsorption step the ion replaces another ion (of a different type) from the exchanger. It is more of a chemical process, while chromatography relies to a great extent upon physical characteristics. Russell and Pearce employed columns of Crystallite having bed lengths up to fifty feet. Only partial separations were obtained. Concentrated rare earth solutions were used which contained more than enough material to saturate the exchanger. They showed that rare earth ions of decreasing radius are held more firmly on the exchanger.

In retrospect, one can see that up until the present time a relatively rapid method for separating the trivalent rare earth ions from each other does not exist. It may be concluded from the preceding discussion concerning the electron configurations of the trivalent rare earth ions that it appears unlikely that a specific reagent will be found for even one of them. It would be much more expedient to investigate new methods of separation than to look for a specific reagent.

c) The principles of chromatography and ion-exchange. Inasmuch as the method for separating the rare earths to be described in this thesis employs the principles of both chromatography and ion-exchange, it becomes apropos to discuss these processes individually and in some detail. Several theories have been advanced to describe each of the processes. Since the theories are developed mathematically, only the results are used in the discourse. The original papers should be consulted for the mathematical treatment, if desired.

Chromatography was discovered by Tswett (33) in 1906 during the course of his research on chlorophyll. When a petroleum ether extract of some dried leaf material was passed through an adsorbing bed of precipitated chalk, two green bands were formed in the column. These bands were later shown to be chlorophyll A and chlorophyll B.

Since that time, chromatography has been applied successfully to an ever increasing number of fields of research. Separations became possible which to this day can not be brought about by any other method. Strain (34) has condensed the laboratory applications of the method under ten main headings:

1) Resolution of mixtures into their constituents.
2) Determination of the homogeneity of chemical substances.
3) Comparison of substances suspected of being identical.
4) Purification of substances.
5) Concentration of materials from dilute solutions.
6) Recognition and control of technical products.
7) Quantitative separation of one or more constituents from complex mixtures.
8) Determination of molecular structure.
9) Combination with electrophoretic separations.
10) Regeneration of substances from complex addition compounds.

The process of forming a chromatogram is dynamic in nature, since there is always a liquid flow and the adsorbed material and eluant are in motion. The solution which contains the material to be adsorbed is first percolated through the column of adsorbent. After the primary adsorption step, the chromatogram is developed by washing the adsorbed material with the eluant solution. The separation is effected through differences in solubility and the

strengths of the adsorption. Relatively high flow rates are advisable, which suggests that adsorption occurs only on the outer surface. If the flow rate of the eluant is slow, diffusion of the material into the adsorbent particles may occur, and the bands are not separable from each other. The third and final step in the process consists of removing each of the bands from the adsorbent. Generally, the material to be adsorbed is dissolved in a solvent in which it is sparingly soluble and which is reactive with neither the material nor the adsorbent.

In chromatography, the procedure that an experimenter uses is still primarily one of trial and error, inasmuch as some adsorbents work where others fail and for no apparent reason. However, the large number of publications in the literature in which descriptions of the method are presented serve to give the experimenter a large amount of empirical knowledge which can be useful in his own research.

The exact nature of the forces which are exerted between the ions or molecules of the adsorbate and the adsorbent are not known. Bradley (35) has discussed the problem but came to no definite conclusions. In static systems, i.e., those in which equilibrium has been reached between adsorbate and adsorbent, Brunauer (36) concluded that more than one type of force is in effect. The conclusion can be drawn that the forces of adsorption are surface forces of some kind or other which do not necessarily

result in compound formation. Considerable theoretical work on the nature of the forces remains to be done.

A theoretical approach to the dynamical chromatographic process has been made by Wilson (37), with an extension to this theory being made by DeVault (38). They assume that there is an instantaneous equilibrium established between the adsorbent and adsorbate, and that the volume of liquid in the interstices of the adsorbent per unit length of column is negligible. A differential equation is developed on the basis of conservation of the material within the column. Boundary conditions are established with the result that the solutions of the equation show the leading edge of the band to be sharp, i.e., the solutions are discontinuous. The solutions to the equation also reveal that the material should trail out on the top, or trailing edge of the band. Hence, the general shape of the elution band is predicted, and this band, when once formed, proceeds down the column of adsorbent at a rate dependent upon the flow rate of the eluant and the adsorption affinities between the materials and the adsorbent. Experimental work which corroborates the theoretical elution curve has been presented by Cassidy (39).

A number of materials have the ability of exchanging some of their ions for other ions. The property of ion-exchange was first reported in the literature in 1850 by Way (40), who noticed the exchange of K^{+} for Ca^{++} in soils.

Since that time, numerous types of clays and other inorganic materials have been found which have exchangeable ions. These materials are broadly called zeolites, and they are generally some form of an alumino silicate with replaceable metal ions. A number of synthetic gel zeolites have been produced commercially for some time which exhibit the same behavior.

Not all ion-exchangers are inorganic in composition. A number of samples of peat and lignite display exchange properties. A process for sulfonating coal has produced a product which has replaceable hydrogen ions. The commercial name of this product is zeo-Karb H (41). The discovery of a substance with a replaceable hydrogen ion had far-reaching effects. The limitations of the ion-exchange method which were inherent with the zeolites were removed. Because of the fact that the zeolites disintegrated in acid solution, they were only usable within a narrow pH range. Heretofore, zeolites were used principally in water softening and in the treatment of soils. The fact that sulfonated coal could be used in a hydrogen cycle increased the number of applications in numerous research fields.

It was discovered quite accidentally by Adams and Holmes (42) that the synthetic resins produced by condensing polyhydric phenols, formaldehyde, and a third compound, containing a desirable functional group, possessed ion-exchange properties. It is the functional group that becomes in-

corporated in the structure of the resulting resin which produces the exchangeable ions. Various functional groups can be incorporated into the resin, the resulting resins being different in their applicability as ion-exchangers. A number of resins have been produced commercially which are suitable exchangers over a large pH range. The functional groups most commonly found in the synthetic ion-exchangers are (1) the nuclear sulfonic acid group for use in strong acid solution, (2) the methylene sulfonic acid group to be used at slightly higher pH values, (3) the carboxyl group which exchanges in slightly acid or neutral solutions, and (4) phenolic hydroxyl groups for use in alkaline solutions. The capacity of a resin which has two or more of these types incorporated in it increases as the pH is raised, since more exchange points become available. To illustrate this point, the nuclear sulfonic acid group exchanges in acid, neutral, or alkaline solution while the phenolic hydroxyl group does not lose its hydrogen in acid solution, but undergoes exchange above a pH of ~ 8.

The synthetic resin Amberlite IR-1* was used as the ion-exchanger for the rare earth separation to be described in the ensuing sections. It is produced by condensing phenol, formaldehyde, and a methylene sulfonate. Of particular interest for exchange purposes in this work is the

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*Manufactured by the Resinous Products and Chemical Company. Philadelphia, Penna.

sulfonic acid group which serves as the principal exchange point in acid solutions.

The theoretical principles underlying the process of ion-exchange are essentially those enunciated in the principle of mass action. If we consider, for the time being, the reaction of the hydrogen form of the resin (HR) with a monovalent cation M^+ , the reaction

$$(HR) + M^+ \rightleftharpoons (MR) + H^+ \qquad (1)$$

proceeds to equilibrium. Increasing the concentration of M^+ in the solution drives the reaction in the forward direction, while a high acid concentration reverses the process.

According to general thermodynamic treatment, the activity of a solid is constant and is assigned unit activity. Taking this into consideration, the equilibrium constant for the reaction (1) can be expressed by

$$K_{eq} = \frac{a_{H^+}}{a_{M^+}} \qquad (2)$$

However, the work of Kerr (43) did not agree with this equation. Instead, better agreement with facts was found when the solid phase components were included in the expression for the equilibrium constant. Vanselow (44) not only considers it necessary to include the solid phases in the equilibrium expression, but states that the activities of the solid phases are equal to their mole fractions. Accordingly, the equilibrium constant for reaction

(1) becomes

$$K_{eq} = \frac{a_{H^+} \frac{MR}{MR+HR}}{a_{M^+} \frac{HR}{MR+HR}} = \frac{a_{H^+}\,(MR)}{a_{M^+}\,(HR)} \qquad (3)$$

which in this case becomes identical to the expression proposed by Kerr. However, for the case where univalent and divalent cations are employed, the reaction and ensuing equilibrium constants are given by (5) and (6).

$$2(HR) + M_2^{++} \rightleftharpoons (MR_2) + 2H^+ \qquad (5)$$

$$K_{eq} = \frac{a^2_{H^+}(MR_2)(MR_2+HR)}{a_{M^{++}}(HR)^2} \qquad (6)$$

Experimental work by Schubert (45) in which multivalent ions were used showed that the valence of the resin must be taken as unity. The proximity of the exchange points in the resin to each other should exert some influence on the ability of a polyvalent cation to undergo exchange.

The mechanisms involved in the process of operating an ion-exchange column have been studied theoretically from several points of view. Beaton and Furnas (46) have applied the theory of heat transfer through a bed of crushed solids (47) to the ion-exchange column. The analogy between the two processes is very close. After an extensive mathematical treatment, the final equations when applied quantitatively to the rare earth problem leave much to be desired. By applying the mass action law, Boyd and Adamson (48) have derived an expression for an adsorption isotherm which considers not only the concentrations of the ions in

solution, but also considers the rate constants for the various reactions involved. The theory of Boyd and Adamson predicts the behavior of a column of adsorbent when it is being operated under non-equilibrium conditions. A large number of theoretical curves are presented which use arbitrary values for the equilibrium constants and the rate constants. The experimental results obtained from their elution curve are compared with the calculated curves. The curve which gives the best fit gives the adopted values for the rate and equilibrium constants.

An approach to the problem of the mechanism of the column process using the equations of diffusion theory has been made by Boyd, Myers, and Adamson (49). Both the case of sphere-like particles and the case of slab-shaped particles are considered. They found that the most important factors in determining the nature of the rate controlling mechanism were the distribution constant K, and the radius of the resin particles. The distribution constant adopted by them is defined by equation (7).

$$K_{dis.} = \frac{\text{amount adsorbed/grams of air dried resin}}{\text{amount in solution/liters of solution}} \quad (7)$$

A large value for K and/or small values of the particle size favor a rate determined by diffusion through a film of liquid at the periphery of the resin particle. While the diffusion equation is independent of the effect of other ions on the rate of adsorption or on the equilibrium point,

it does not permit one to calculate the isotherm slope or distribution coefficient. It is concerned only with the manner in which equilibrium is realized.

Mayer and Tompkins (50) have developed a theory which is based upon the column behaving like a distillation column. Their theory reputedly predetermines the necessary operating conditions so that any degree of separation of two elements can be achieved. The theory entails a knowledge of the number of theoretical plates comprising the column and the distribution coefficient for each of the ions in the mixture to be eluted.

In concluding this section in which the various theories of ion-exchange have been briefly described, it would probably be apropos to mention that considerable work still remains to be done in developing an experimental technique which will produce exactly reproducible total elution curves from one experiment to another. The separation curves are quite reproducible, but the shapes of the total elution curves are just enough different from each other so that the experimental data can not be utilized in the testing of the various theories mentioned above. As matters stand now, a proper choice of values to be used in the theoretical equations could only come from a statistical average.

III A Statement of the Problem

At the time that the experimental work to be pre-

sented in this thesis was initiated, the reports from the group at Oak Ridge that was working on this problem had merely indicated that the cerium and yttrium activities (produced in uranium fission) are partially separated from each other on an Amberlite IR-1 column when eluted with citric acid. The purpose of this research will be directed toward the application of an ion-exchange process for separating micro and macro amounts of pure rare earths in which ammonia treated citric acid is the eluant. A preliminary investigation was first initiated to determine the variable factors which affect the efficiency of the separation process. A systematic study of each of these variables, one at a time, led to a set of conditions, which, when properly employed, gave an efficient process for preparing pure rare earth compounds.

EXPERIMENTAL PROCEDURE

I The Apparatus

The principal piece of apparatus consists of a glass tube filled with resin. The glass column is mounted in a vertical position by means of clamps. The bottom end of the glass tube has a tapered shoulder with a stop-cock or screw clamp connection to adjust the flow rate of the eluant. The resin is kept in the tube by either having a plug of glass wool at the bottom or sealing a porous glass disc in the lower end. The resin is pre-soaked in water to get out of the air bubbles out of it. It is then added to the column until it occupies about two-thirds of the total length of the column. A glass reservoir containing the citric acid solution used as eluant is connected to the top of the column so that one can use simple gravity flow in passing the eluant through the column.

A number of experiments were conducted in which radioactive tracers were used in the absorbed material on the column. In order to determine the position of the material on the column at any time during the experiment, a portable ionization chamber was constructed which in turn was connected to a counting circuit and scaler by long leads. This made the ionization chamber quite portable. The counting tube was a conventional cylindrical silvered glass flow and probe type tube. The tube was housed inside a cylindrical copper

tube to shield it from any stray beta radiation. The instrument was used only qualitatively -- to locate the position of the activity in the column.

The samples of eluate which contained radioactivity were measured for their activity on a Lauritsen quartz fiber electroscope. A multiple stage mounting was erected directly beneath the ionization chamber so that the position of geometry could be reproduced. With this instrument, the maximum activity which could be read accurately was $\sim$ 100 divisions per minute. Background activity for this particular instrument was 0.15 div./min. When the activity in the eluted samples would approach the maximum value, the samples were transferred to a stage further removed from the ionization chamber of the electroscope. The measured activity was decreased because of the decrease in the solid angle between sample and electroscope and also because of the introduction of an added air space which in turn absorbed a percentage of the radiation. Conversion factors for the individual radioactive isotopes used were established between the various sample mounting platforms to facilitate the measurement of the extremes of activity in the various samples.

In the experiments in which the analyses were conducted spectrophotometrically, a Beckmann Quartz Spectrophotometer was employed. This instrument covers a spectral range from 220 mu to 1200 mu. From a knowledge of the

dispersion of the quartz optics as a function of the wavelength (furnished with the instrument by the manufacturer) a chart was constructed in which the slit width of the instrument was plotted as a function of the wave length of the light for any constant spectral band width. In this manner it became possible to reproduce the optical densities for a given concentration of a particular ion species. Recourse had to be made to the method using a constant spectral band width because of the sharpness of the rare earth adsorption bands. For readings above 620 mu the band width employed was 2mu, while below 620 mu the band width was maintained at 0.5 mu. Use of the narrow spectral bands for illumination of the samples increased the sensitivity of the measurement of the sharp absorption bands of the rare earths.

II Materials

A stock solution of inert cerium carrier which was used in a number of experiments was prepared from pure ammonium hexa-nitrato cerate* which was dissolved in water, with a few drops of sulfuric acid added. The resulting solution was heated to boiling and sulfur dioxide passed in to reduce the cerium to the trivalent state. The resulting solution was made ammoniacal to precipitate cerous hydroxide.

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* Manufactured by G. F. Smith Chemical Co., Columbus, Ohio.

After filtering, the precipitate was dissolved with dilute sulfuric acid and stored. Gravimetric analyses were conducted on small aliquots of the stock solution to determine the concentration.

The yttrium tracer which was used was obtained from commercially pure yttrium chloride[1] with a specified purity of >80%. No attempts were made at this point to further purify the material before using it in an elution experiment.

The original starting material used in the experiments with neodymium, praseodymium, and samarium was from a stock of commercial didymium.[2] Inasmuch as the composition of didymium is variable, the particular lot of material used in this work was analyzed spectrophotometrically and was found to contain 78% Nd, 18% Pr, and 2.5% Sm. The remainder consisted of small amounts of Ce and La along with traces of many of the other rare earths. In general, commercial didymium is principally a mixture of Nd, Pr, and Sm in which the ratio of Nd to Pr is 2:1. The samarium content usually varies between 1-12%.

The heavy rare earths were obtained from several of the native minerals. Large samples of gadolinite,[1] risörite,[3] and blomstrandine[3] were treated with 6N nitric acid to

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[1] A. D. MacKay Chemical Co., New York, N. Y.

[2] Lindsay Light and Chemical Co., West Chicago, Ill.

[3] Wards Scientific Foundation, Rochester, N. Y.

extract the rare earths. A crude separation of the light fraction (cerium earths) from the heavy yttrium earth group was conducted by Mr. Porter, using a double sulfate precipitation with potassium sulfate. An additional supply of rare earths containing principally samarium and gadolinium oxides was obtained from Lindsay Light and Chemical Co. which also contained 8% Dy, and ~10% of all the other rare earths as impurities (mostly yttrium).

The citric acid was of ordinary commercial grade. A spectrographic analysis of the ash after igniting some of the material showed only traces of any metals. The solid acid was in the form of the mono-hydrate.

The oxalic acid used as a precipitating agent was Merck's C. P. grade. An analysis of the ash after ignition showed no contaminating metal ions. (A contaminating ion would be one which would form an insoluble oxalate).

The radioactive tracers used were isotopes of cerium and yttrium produced in uranium fission.

III A Brief Description of an Experiment

The glass column is clamped in a vertical position and half filled with water. The dry resin is sieved to 40 mesh size and pre-soaked in water for several hours to remove a large part of the adhering gas bubbles. A slurry of the resin is poured into the column until a height of one foot of settled resin is obtained. The resin in the column is then backwashed with water. (Backwashing means the

process of making the liquid flow through the column in an upward direction). The process of backwashing serves to classify the resin according to particle size, break up any lumps that may form through packing, and to eliminate the fines. Additional, similar amounts of resin are added with subsequent backwashing after each addition. Proceeding in this manner, the resin bed can be classified properly in a much shorter time and without any danger of the resin becoming packed in the column, either before or during an elution experiment.

The resin is conditioned by alternately changing it from the hydrogen cycle to the sodium cycle several times. A five per cent solution of hydrochloric acid is passed through the column to convert the resin to the hydrogen form, while a five per cent solution of sodium chloride when passed through the column will convert the resin to the sodium form. Tests are made on the eluate to see that the resin has been completely converted from one cycle to the other before the solutions are changed. The minimum contact time for each solution with the resin is thirty minutes. The conditioning step serves to elute any foreign ions which may be incorporated in the resin by previous handling.

The sample to be adsorbed on the resin is prepared from a weighed amount of the rare earth oxide by dissolving the sample in a slight excess of the calculated amount of 6N hydrochloric acid. After dissolution of the sample is

complete, it is diluted to several liters volume and the pH adjusted to the region between 1.8 and 2.5. The solution is passed into the resin column at a flow rate of 1.5 $cm.^3$ per $cm.^2$ of cross-sectional area per minute, the resin being initially in the acid cycle. The rare earth ions in solution exchange places with the hydrogen ions at the top of the resin bed, converting that part of the resin to MR_3. After the sample has been placed on the column, the column is flushed with water and is then ready for the desorption step.

The column is generally operated under the conditions prescribed for the particular experiment as pertains to the flow rate and pH of the eluent. For anything near reproducible results the initial starting conditions must be strictly maintained throughout the course of the elution. A running log is kept of the volume of eluent passed through the column. The pH of the effluent is periodically measured to observe the point when the resin has been converted completely to the ammonium form. At this time, the pH of the effluent rises sharply until it has the same value as the influent. No breakthrough of the rare earths is to be expected until after this change of affairs has taken place. The samples of effluent are collected in volumetric flasks or some other suitable means of determining volumes, and then transferred to beakers. If radioactive isotopes are being used, a one milliliter aliquot is removed for analysis. The rare earths in the beaker of solution are precipitated as the

oxalates by adding oxalic acid (10 grams/liter) and allowing at least three hours for complete precipitation before filtering. The precipitate settles out much faster if the solution is heated above 75°C after adding the oxalic acid. The filtered samples are then ignited to the oxides and weighed. By plotting the grams/liter of oxide vs. volume of eluent passed through the column, one can determine the total elution curve. Directions for the analysis are given below in part IV of this section.

When the elution has proceeded long enough to furnish the information desired from the experiment, the remainder of the material on the column can be removed rapidly by raising the pH of the influent citrate to a pH of approximately 5.0. At this pH the rare earths exist only as a complex in solution and will not exchange with the ammonium form of the resin.

The stripped resin is put through a number of reconditioning cycles of HCl and NaCl as mentioned previously. The procedure of backwashing is repeated to break up any resin agglomerations which may have formed during the course of the previous experiment. The column is now ready for another experiment.

According to the manufacturer, the exchange properties of Amberlite IR-1 do not change with time or with the frequency of use. In the course of this work it was necessary to change the resin after three or four experiments,

because of the growth of mold in the resin. This will be discussed more fully in a later section.

IV Methods of Analysis

The methods of analysis which were used for the various rare earth ion constituents, depended in a large part on the particular experiment being undertaken and the particular rare earths involved. All of the methods used employed physical means to establish the amount of each of the rare earths in the mixture. These were (1) the determination of the radioactivity of a sample from a knowledge of the specific activity of the starting sample and (2) the use of a Beckmann Quartz Spectrophotometer to measure the intensity of an absorption band in the spectrum as a function of the concentration of a given rare earth ion in the solution.

For the most part, the radioactive method of analysis is quite sensitive, the sensitivity being directly proportional to the amount of activity put into the starting sample. The activity was obtained from a stock solution of a radioactive isotope of the element under investigation. This procedure was used in the experiments with cerium and yttrium.

The radioactive isotopes were produced in the Clinton pile by the fissioning of a uranium slug with slow neutrons. The metal was dissolved in nitric acid and further treated by

a process developed by J. A. Ayres (51). This process employs an ion-exchange column on which all of the fission products are adsorbed. By percolating specific reagents through the column one can elute various groups of radio-isotopes. One of these groups consists of the trivalent rare earths and yttrium.

After a period of several months of decay, only the 57 d Y^{91}, the 28 d Ce^{141} and 276 d Ce^{144} isotopes remain. All of the other activities in this group which were produced in the fission process have long since decayed to stable isotopes.

The chemical separation of the cerium and yttrium from each other is quite simple. Both of these elements have a trivalent state in which their chemical properties are very similar. However, cerium also has a tetravalent state that is stable in aqueous solution which can be used for a quantitative separation. With small amounts of yttrium and cerium carriers added, the cerium was oxidized to Ce^{++++} with bromate, and precipitated with potassium iodate. The precipitate was treated with hydrazine to destroy the iodate, and inactive yttrium carrier introduced. The precipitation cycle was repeated until an aluminum absorption curve of the radioactive cerium isotope showed no yttrium activity to be present. This was the criterion for purity. The active yttrium in the filtrate was treated with hydrazine to destroy the excess bromate and iodate, more inactive

cerium added, and the precipitation cycle for cerium repeated until an aluminum absorption curve of the yttrium activity showed it to be pure.

The stock solutions of the radioactive isotopes separated from each other in this manner were diluted with water to a two liter volume. The amount of activity per milliliter of stock solution was obtained by withdrawing a one milliliter sample and diluting it to 100 milliliters with water. A one milliliter aliquot of this latter solution was withdrawn and evaporated on a watch glass. Decay curves and absorption curves through aluminum were made periodically to test for purity and to use as a set of standards for the numerous experiments to be performed.

It can be seen, then, that in an actual experiment in which 250 milligrams of inactive yttrium is mixed with ten milliliters of the active yttrium stock solution, the additional amount of radioactive yttrium added is negligible as regards an actual weight assay. From the known mass of material used in an experiment, and the amount of activity (measured in divisions/min.) added to the inactive mass, the activity per milligram can be computed. Hence, in the course of an elution if a known volume of eluate is measured for its activity, the activity in turn can be transposed into milligrams. Thus a very sensitive means of assay is realized, much more sensitive and accurate than a chemical method since there are no solubility losses. In the normal course of

analyzing the fractions gravimetrically, large experimental errors are introduced through the solubility of the rare earths, particularly with the front and tail fractions. Frequently, in those fractions the concentration of rare earths is less than 10 milligrams/liter of eluate.

The one milliliter sample of eluate to be measured with the electroscope is pipetted from a volume element and deposited on a watch glass. The sample is dried by placing it under a heating lamp, the distance from lamp to sample being about twelve inches. If the lamp is brought much closer than this distance the heat causes a partial decomposition of the citric acid. This results in considerable frothing and bubbling, and the observed activity measurement can no longer be considered as the true reading which would be obtained under normal conditions. Drying the sample in this manner requires one or two hours, which amount of time must elapse anyway so that the 17 min. Pr^{144} daughter of the Ce^{144} isotope will have grown back into the sample in equilibrium quantities. (This takes about seven half-lives of a short lived daughter activity of a long-lived parent activity.) The energies of the various beta emitters used are sufficiently high so that self absorption of the radiation within the sample does not introduce any recognizable error.

In measuring the activity of the samples with the electroscope, the geometry of the mounted samples must be

reproduced. A number of brass plates, 3" x 3½" were made which could be slid into a fixed position under the ionization chamber. The watch glass containing the dried sample is centered on the brass plate and placed in position under the electroscope.

In using the radioactive assay method to the best advantage, one must consider both the energy and the half-life of the isotopes. Energy and half-life are somewhat inter-related, the isotopes with long half-lives emitting the less energetic beta particles. For the purpose of the elution experiments to be described, which in some cases required as much as a week to perform, it is more advisable and accurate to work with those isotopes which have periods of at least seven days. When the half-lives are seven days or longer the amount of correction in the measured activity which must be made to take into account the natural decay of the isotope before converting into milligrams is minimized. The correction is made in the following manner: the standard sample (see above) is read over a period of days to follow the natural decay. The best straight line is drawn through the points when the log of the activity is plotted as a function of time. An arbitrary zero time, t_o, is chosen to which the activities of the samples measured at the time t are referred. From equation (8)

$$\frac{\text{activity of standard at } t_o}{\text{activity of standard at } t} = \frac{\text{activity of sample at } t_o}{\text{activity of sample at } t} \quad (8)$$

it becomes a simple matter to calculate the activity in any

sample at the time t_o when read at the time t. Knowing the number of milligrams of material that one division per minute of the standard on the electroscope represents at the corrected time t_o, the activity of all the samples can be converted directly into milligrams.

When the half-life of a beta active isotope is of the order of thirty days or longer, the energy associated with the electron is generally less than one mev. Such is the case with the Ce^{144} isotope. The energy of the beta particles from this isotope are 0.35 mev, which is too low an energy to read accurately with the electroscope because of the large errors introduced through self-absorption of the radiation within the sample. However, the Ce^{144} decays to 17 min Pr^{144} which emits a 3.07 mev beta particle. The Pr^{144} daughter is allowed to grow to equilibrium with its Ce^{144} parent and is then measured on the electroscope, using an aluminum foil to absorb all the radiations from the Ce^{144} nuclei, while those beta particles from the Pr^{144} are actually measured. Thus one can see that in this manner, the actual decay rate is that of the Ce^{144} isotope. In the specific case at hand, the range of the Ce^{144} beta particle is $\sim$ 70 mg./cm.^{2} aluminum. The samples containing cerium activity were measured through a 70 mg./cm.^{2} aluminum absorber. In this manner of measurement, a fluctuation of one or two mg./cm.^{2} Al in self absorption within the sample would produce only a small error in measuring the energetic

beta, whereas it could produce an error of ~20% if the soft beta ray was being measured.

The remainder of the rare earths do not have readily available isotopes which occur either in fission or through some artificial bombardment scheme. Hence, recourse was made to the use of a Beckmann Quartz Spectrophotometer for the analysis. The rare earth elements whose trivalent ions possess suitable absorption bands for analytical purposes are Nd, Pr, Sm, Gd, Er, Ho, Tm, and Yb. To establish a set of extinction coefficients for the various absorption bands, pure materials must be had. However, the only pure materials which were available at the start of the research were salts of neodymium, praseodymium, and samarium, obtained on loan from the private collection of Dr. F. H. Spedding.

In the numerous experiments in which commercial didymium was used, analyses were necessary for only the three main constituents, Nd, Pr, and Sm. A large column was erected to produce relatively large amounts of Sm-Nd fractions free from Pr, and Nd-Pr fractions free from Sm. The column had a bed length of 850 centimeters and a diameter of 49 millimeters. Before the large column was erected for use with didymium, the experiments with cerium and yttrium had, for the most part, been completed. A crude small scale experiment using a small column and two grams of didymium (as oxide) showed a partial separation and the order of elution to be Sm, Nd, and Pr. The purpose of the large

column was to produce mixtures in which there were but two main constituents and to have them in near equal concentration.

To establish a set of molar extinction coefficients, the oxides of the pure rare earths were dissolved in 5% hydrochloric acid and diluted to a definite volume so that the concentration in moles per liter of each solution was known. The complete spectrum from 340 mu to 1000 mu was measured for each of these species, and those absorption peaks were chosen for future analytical purposes which were (1) the most intense, (2) free from interference through having an absorption band in common with another rare earth, and (3) followed Beer's Law. The absorption bands of neodymium which were chosen for analytical purposes were those at 740 mu and 795 mu, the extinction coefficients being 6.13 and 7.9 respectively when a spectral band width of 2 mu was employed. In a similar manner, the spectrum of Pr showed the best band to be that at 444 mu with an extinction coefficient of 6.20. With Sm, the best band is at 401.5 mu, the extinction coefficient being 3.38.

In the course of analyzing samples eluted from the column, it is not necessary to dissolve an accurately weighed sample in a definite volume of solvent in order to determine the concentration. It is much more simple, and accurate, to place the analysis on a relative basis, since it is known at the outset that the only rare earths present

are Nd, Pr, and Sm. By measuring the optical density of an absorption peak with the spectrophotometer and applying Beer's Law, one can calculate the concentration of that ion species in the solution. The concentrations of all of the species in the sample are totaled, and the fraction of the total for any particular ion species represents its amount in the mixture. In this manner, it is not necessary to weigh out a sample, or even to dilute the solution to a known volume. The solutions were roughly made up to contain 100 milligrams of oxide in ten millliliters of solution. To increase the sensitivity in those samples which were suspected of having only small amounts of a particular ion, the above concentration can be increased.

The procedure had to be modified somewhat in those experiments employing heavy rare earths. This group is generally considered to consist of Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. Of these, Tb, Lu, and Y possess no absorption bands which can be used for analysis. However, pure salts of the other members of the sub-group were not available for use in determining the respective molar extinction coefficients. By adopting a uniform concentration of sample of 200 milligrams of oxide dissolved in ten millliliters of 5% hydrochloric acid and then measuring the absorption peaks, one can get a fair estimate of the elution curves of each individual ion species.

The spectrum of gadolinium lies entirely in the ultra-

violet, two sharp peaks being utilized, at 272 mu and 275.6 mu. Since the best samples of gadolinium which have been prepared contain, at most, no more than a few per cent of other rare earths, the extinction coefficient can be taken as 2.1 for the 272 mu peak.

A sample of ytterbium was extracted with 0.5% sodium amalgam and its molar extinction coefficient determined as 1.63. The Yb^{+++} ion possesses only one absorption band, at 973 mu, which unfortunately coincides with a strong absorption band of erbium at 976 mu. For this reason, ytterbium can be determined spectrophotometrically only in those samples which are free from erbium or contain only small amounts. A qualitative estimate can be gathered of the ytterbium content from the known ratio of the optical densities of the 653 and 976 mu peaks for erbium. In any sample, both the 653 and 976 mu peaks are measured, and from the known ratio, the 976 mu peak is calculated for erbium. The difference between the observed and calculated value of the optical density at 976 mu is due to the ytterbium in the sample.

The extinction coefficients for Dy, Tm, Er, and Ho were obtained from the data published by Rodden (52). These are: for Dy, the absorption band at 910 mu, with $\epsilon = 2.73$; for Er at 522 mu, $\epsilon = 4.0$; for Ho at 541 mu, $\epsilon = 2.75$; and Tm at 684 mu, $\epsilon = 2.24$.

In an analysis, the undetectables, Y, Tb, and Lu, are grouped together and determined by difference. In the

200 milligrams/10 milliliter sample of the heavy rare earths, the concentrations of the components (obtained by use of Beer's law) are converted to milligrams of oxide, the total being subtracted from 200 to give the amount of undetectable ions in the sample. Since lutecium is quite far removed from yttrium and terbium in the order of elution from the ion-exchange column, the above method can actually be used in practice, at least in a qualitative way.

V Calculation of the Data

After the chemical analyses have been completed, the total elution curve, and the individual elution curves can be drawn. The separation can be shown to better advantage if two additional graphs are drawn from the data on the elution. These will be referred to as a "separations" curve and a "purity" curve.

The total elution curve is that curve which results when the mass of rare earth (as oxide), eluted in a given volume element is plotted as a function of the volume of eluant passed through the column. The area under this curve represents the amount of material eluted. The individual elution curves can either be drawn directly (as is the case when radioactive tracers are used) or the proper percentage of the total weight can be used as determined by the spectrophotometric analysis. In the experiments with yttrium and cerium using radioactive tracers, only one

activity was introduced into the starting mixture. Thus, one used radioactive yttrium plus inactive yttrium plus inactive cerium, or inactive cerium and yttrium plus radioactive cerium. When a radioactive isotope is used, the total elution curve is obtained from gravimetric data, the individual elution curve of each component being determined through its activity, while the amount of the second component in the mixture can be obtained from the difference between the two curves.

The method of analyzing the samples containing neodymium, praseodymium and samarium, for which the molar extinction coefficients are known, has been outlined above. When the percentage composition of each ion species in the sample has been determined, recourse is made to the total elution curve. Each sample is marked by a volume interval along the abscissa. The midpoint of this volume interval is taken and the corresponding value of the ordinate along the total elution curve is recorded. The proportionate amount of the ordinate as determined from the percentage composition of the total sample is plotted for each ion species. This procedure is repeated for a number of samples. The line joining the points for each rare earth ion represents the individual elution curve of that ion.

The same procedure was used with the heavy rare earths except that all of the undetectable ion species must be grouped into one value. This procedure was described

more fully in the preceding section.

The "separation" curve shows the percent of a particular ion species which is eluted as a function of the volume of eluant. After the individual elution curve is determined, the area under the curve from the breakthrough to any specified volume of eluant represents the amount of the ion which has been eluted to that point. In this manner it is not necessary to carry the elution to completion in order to determine the per cent eluted. If, in the course of the elution, a separation is effected, the degree of the separation can be illustrated by plotting the per cent of an ion type eluted as a function of the volume. This is done for each species. The farther the curves are from each other, the better the separation. However, in those experiments in which the starting sample consists of predominately one element, this means of presenting the data loses significance. Nowhere in a plot of this kind is the composition of the starting material considered. Consequently, a "purity" curve was devised to more adequately express the degree of separation.

Instead of plotting the per cent of an ion eluted as a function of the volume, it is plotted as a function of the "purity" of the sample. The "purity" is defined as the composition of all the material eluted to any specified volume. To determine the value of the purity, the area under the total elution curve is measured from the break-

through to a specified volume. In a similar manner, the area under the individual elution curve is measured from its point of breakthrough to the volume in question. The per cent purity of ion species A at the volume V is calculated by the expression

$$\frac{\text{mass of A eluted}}{\text{total mass eluted}} \times 100 = \% \text{ purity of component A} \quad (9)$$

The procedure is repeated over a considerable portion of the total elution and a graph is made by plotting the per cent purity of the component against the per cent of that component eluted. The line connecting these points shows the purity of the material eluted at any point during the course of the elution.

A purity curve of an idealized elution of two components in which complete separation is obtained would appear as follows: the curve for the first component would proceed at 100% purity until it was all eluted; subsequently the purity would drop slowly to the composition of the original sample. The second component would start at zero purity and remain at this value until its breakthrough. The purity of this component will then gradually rise until it becomes equal to its purity in the original sample.

In the elution of a binary starting mixture, a good separation of the first component eluted assures at least a high enrichment of the second component in the later fractions. Hence, in performing an experiment, it was not

necessary to complete the total elution as the most pertinent information can be obtained from the fractions which often represents only the first 75% of the total starting material. If the experiment is designed to produce that material which becomes rich in the tail fractions, then the elution must be continued with a much larger volume of eluant.

The areas under the elution curves were obtained either by counting the squares within the area concerned, or by utilizing a polar planimeter which gave rapid and accurate results. In the event that the volume of eluant used was large, and large amounts of material were employed, the graph obtained was too large to read with only one or two sweeps of the planimeter. It was found to be more expeditious to use the old method of counting squares and estimating those areas which did not encase an entire square.

EXPERIMENTAL STUDIES

I The Method of Attack to the Problem

While the investigations under way at Oak Ridge by Boyd, Cohn, and co-workers were directed toward producing pure tracer activities, the present work was initiated to determine the feasibility of applying the ion-exchange method to the production of pure rare earths in multiple gram quantities. The first thought and consideration was given to achieving this end by the use of large and long columns. Since the terms of producing macro amounts could be extrapolated from small scale experiments, the research became one in which the factors governing the elution could be investigated one at a time.

Of the many factors affecting the elution, not all were foreseen immediately. Instead, one set of experiments led to another, revealing and suggesting the need for further experiments. The work was designed to investigate, one at a time, the variable factors. The particular value or range of values for each variable which gave the highest percentage of pure material was recorded, to be used in compiling a set of conditions which would give high yields of pure product in reasonable periods of time. In doing this, the assumption was made that each variable is independent of the others and that the net effect is additive.

The first sets of experiments were performed using individual tracers to check the reports that were emanating at Oak Ridge. As these experiments would also provide experience in manipulating ion-exchange columns, it was felt that the time spent in developing a technique was justified. Elutions of individual tracers and subsequent experiments using mixtures of tracers were carried out, as will be described in the next section. When these experiments were completed the methods for analysis had been fairly well standardized so that the work with macro amounts could proceed.

II Resumé of Work with Cerium and Yttrium Tracers

A number of preliminary experiments were performed in this laboratory by Mr. N. R. Sleight in which only pure tracer was eluted from an ion-exchange column. At first, pure yttrium tracer was used, and then the experiment was repeated under identical conditions using cerium tracer. In one series of experiments, the pH of the citric acid eluant was varied over the range from 2.62 to 3.04 with an uniform linear flow rate of one centimeter of column length per minute, using columns which were sixty centimeters long and one centimeter in diameter. Analyses were conducted by measuring the activity with the electroscope. The results showed that yttrium was eluted quite satisfactorily over the entire pH range investigated, although the actual shapes of the elution

curves differed. At values below pH 2.81, cerium was not eluted very rapidly. The data, therefore, indicated that a separation of the two components could be effected using the ion exchange method.

In a column of resin of this size, the actual amount of rare earth used in the above experiments is negligible. If a mixture of rare earths was used in tracer amounts ($\sim 10^{-9}$ grams) each rare earth species would behave independently of the others in the desorption step. It is then acceptible to superimpose the elution curve for yttrium tracer upon the corresponding cerium elution curve and so make comparisons. The conclusion was drawn that pH 2.75 would probably give the maximum separation for tracer amounts of material using 5% citrate. An increase in the length of the column would tend to magnify the degree of separation.

The elution of each tracer was conducted at a pH of 2.75, using citrate concentrations of 5 and 20%. The elution curves are shown in Figure 1. At this pH value, it is evident that the elution curves of cerium and yttrium are practically super-imposable when 20% citrate is used. The peak of the yttrium curve with 20% citrate was at 269 div/min/ml.

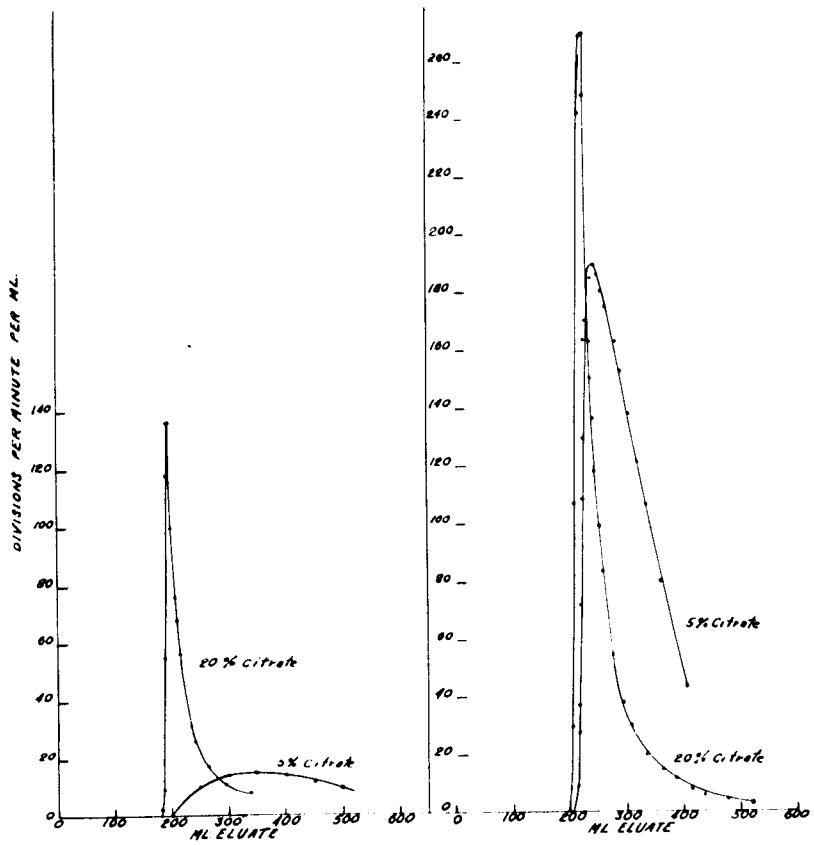

Figure 1. The elution of Ce and Y tracers with 5% and 20% citrate solution: pH 2.75; bed length 1 cm. x 60 cm. Cerium curves on the left, yttrium curves on the right.

III The Separation of Macro Amounts of Cerium and Yttrium

a) The effect of pH. In the preceding section it was demonstrated that a separation of cerium from yttrium can be effected with tracer amounts of material. The same procedure was applied in which macro amounts of material were used. Keeping in mind the fact that the pH of the eluant would have a strong influence upon the separation, the pH range investigated was from pH 2.50 to 2.87. At pH of 2.87 both cerium and yttrium were eluted rapidly with the result that the separation was not as good as the separation obtained at lower pH values. As the pH of the eluant was lowered (other variables held constant) the separation improved, but the amount of eluant and the time required for an experiment increased enormously. At a pH of 2.50 the time necessary for the experiment makes the process impractical.

Three columns were prepared, each one with a bed length of 185-200 centimeters and a diameter of sixteen millimeters. Active tracer of either element was added to the rare earth mixture. Only one activity was used in each experiment because of the fact that the two individual elution bands overlap.

The starting sample consisted of 250 milligrams of cerium, 250 milligrams of yttrium, and either 57d Y^{91} or 275d Ce^{144} tracer, depending upon the particular experiment. The above weights are calculated as metal. Through use of the portable ionization chamber, it was found that the ma-

terial was confined to the top fifteen centimeters of the resin bed in the initial adsorption step. The flow rate of the citrate solution in the desorption-elution process was maintained as close as possible to five centimeters of column length per minute. The eluant was collected at suitable volume intervals, depending upon the experiment and the particular portion of the total elution curve. Since the starting sample sizes in this series of experiments remained the same, the pH was the factor which determined the volume interval taken. The procedure for analyzing the samples has been outlined previously.

The pH values used in the present set of experiments were 2.50, 2.60, 2.66, 2.77, and 2.87. The results are presented in tabular form in Tables 1 and 2, and are plotted as functions of the volume in Figure 2.

Considering the fact that all of the other variables were held constant, it can be stated that the separation of cerium and yttrium from each other is highly dependent upon the pH of the eluant. One can read directly from Figure 2 the amount of yttrium which is eluted before the cerium breakthrough for each pH value. When the starting sample contains equal amounts of the components, a plot such as that in Figure 2 gives a good index of the extent of the separation.

For the conditions of these experiments, the five per cent citrate used as eluant effected a greater separation as the pH was lowered, reaching an optimum value between 2.60

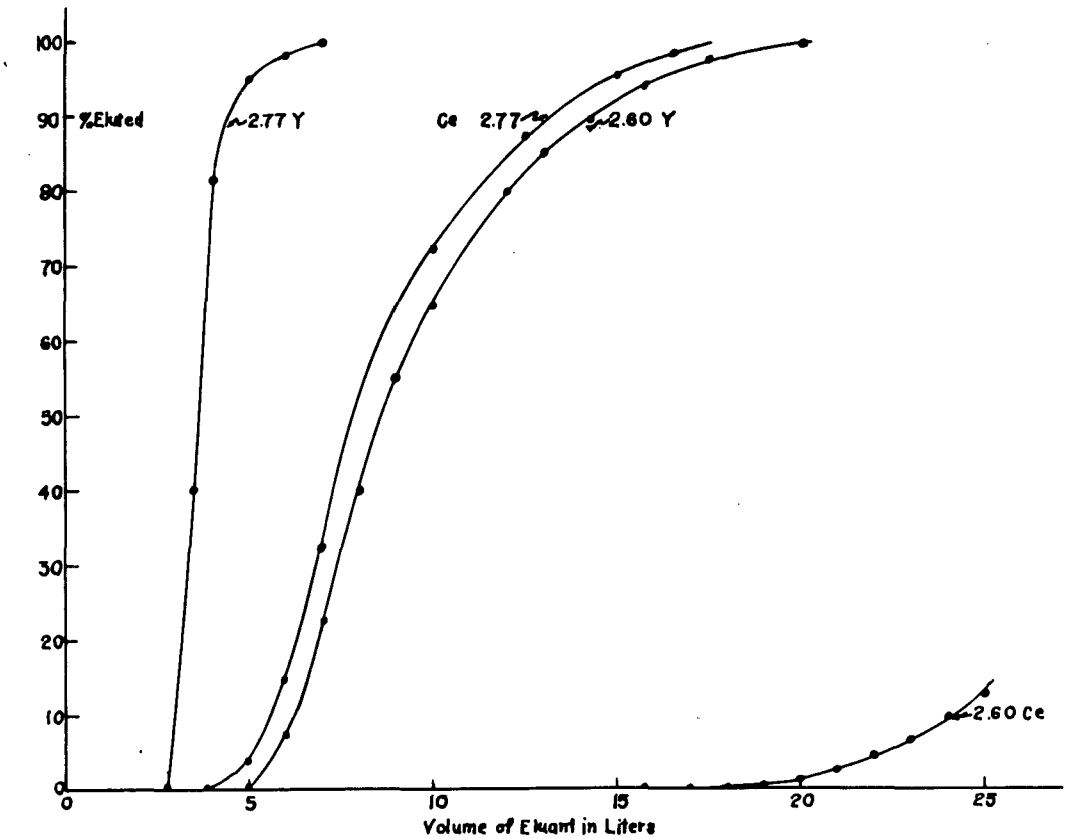

Figure 2. The separation curves of Ce and Y at pH 2.60 and pH 2.77. Weight of sample, 250 mg. each of Ce and Y; column dimensions 16 mm x 185-200 cm.; flow rate, 5 cm/min.

and 2.66. The low pH of 2.50 retarded the breakthrough of both ion species, but the separation was not as good as at pH 2.60 because of the considerable overlapping of the bands. In an elution series which is based upon differences in the basicities of the rare earth ions, (cerium and yttrium are separated by praseodymium, neodymium, 61, samarium, and europium), it might be expected that the pH of the eluant should probably be lower than 2.66 if a separation between these intermediate elements is desired, and possibly still lower if the elements in question are neighbors.

TABLE I

THE EFFECT OF pH OF THE CITRATE ELUANT ON THE SEPARATION

2.50 (a)			2.61 (b)			2.66 (c)			
Liters Eluate	Per Cent Y	Eluted Ce	Liters Eluate	Per Cent Y	Eluted Ce	Liters Eluate	Per Cent Y	Eluted Ce	Lit Elu
10	1.6	--	5	1.0	--	4	2.6	--	
12	15.3	--	7	22.8	--	6	47.6	--	
14	37.5	--	9	54.8	--	8	77.5	--	
16	57.5	--	11	74.0	--	10	91.3	--	
18	69.5	--	13	85.4	--	12	98.3	0.0	
20	77.1	--	15	93.9	--	14	--	1.6	
22	82.3	--	17	97.4	0.1	16	--	6.6	
24	85.6	--	19	--	0.7	18	--	17.3	1
26	87.9	--	21	--	2.5	20	--	30.1	1
28	89.6	--	23	--	6.5	22	--	42.2	1
30	91.0	--	25	--	13.1	24	--	53.2	1
31	--	Ce starts	27	--	21.2	25	--	58.2	2
			29	--	29.3				
			30	--	32.5				

(a) Ce and Y tracer added
(b) (c) (d) Ce tracer added, Y determined by weight of Oxide
(e) Ce tracer added and Ce determined by titration, Y by wei

E I

HE SEPARATION OF Ce AND Y IN MACRO AMOUNTS

c)	2.77 (d)			2.87 (e)		
nt Eluted Ce	Liters Eluate	Per Cent Y	Eluted Ce	Liters Eluate	Per Cent Y	Eluted Ce
--	3	15.1	--	3	58.0	4.6
--	4	18.9	--	4	92.5	16.4
--	5	95.0	3.1	5	99.5	35.8
--	6	98.5	14.2	6	100	54.3
0.0	7	99.7	31.7	7	--	68.2
1.6	8	100	48.5	8	--	77.9
6.6	9	--	71.9	9	--	84.7
17.3	10	--	84.3	10	--	89.8
30.1	12	--	91.6	12	--	96.2
42.2	14	--	98.8	14	--	99.5
53.2	17	--	100	16	--	100
58.2	20	--	--	--	--	--

weight of Oxide
ation, Y by weight of Oxide

TABLE 2

THE PER CENT Y ELUTED BEFORE CERIUM BREAKTHROUGH

pH	Per Cent
2.87	70.0
2.77	82.0
2.66	96.
2.61	98.5
2.50	91.

b) Elution of tracer yttrium from macro cerium. Even though it has been shown that cerium and yttrium can be separated from each other when they are present in equal amounts in the starting sample, it was of interest to study the separation when a small amount of one species is present in a relatively large amount of the other component. Such an investigation is important for two reasons: (1) to see if there is a limit to the degree of purity of a sample, and (2) to see if a multiple column or a multiple cycle process would be feasible. If it were discovered that, in a starting mixture which contained, say, 99% cerium and 1% yttrium, the yttrium was eluted over the whole range of the cerium band, then the process could not be expected to produce spectroscopically pure material.

In the experiment to be described, approximately ten milligrams of yttrium plus tracer, and 250 milligrams of cerium were adsorbed on a sixteen millimeter column with a

bed length of 150 centimeters. The citrate eluant was at pH of 2.77. As before, the yttrium was analyzed by measuring the activity and the cerium by weighing the ignited oxide. The results are presented in Table 3 and in Figures 3 and 4.

The cerium elution curve in Figure 3 is actually the total weight elution curve, inasmuch as the weight concentration of the yttrium before the visible breakthrough of material lies within the solubility range of $Y_2(C_2O_4)_3$ in 5% citric acid solution. This serves also to point out the advantages of a tracer method for detecting small amounts of material.

TABLE 3

SEPARATION OF 10 MG Y AND 250 MG Ce BY ELUTION WITH 5 PER CENT CITRATE, COLUMN LENGTH 160 CM, FLOW RATE 5CM/MIN, pH 2.77

Liters of Eluate	% Y Eluted	% Ce Eluted
3	23.1	--
4	61.0	--
5	85.3	2.8
6	94.8	13.8
7	98.6	28.4
8	99.8	41.8
9	100	53.4
10	--	62.8
12	--	76.0
14	--	83.1

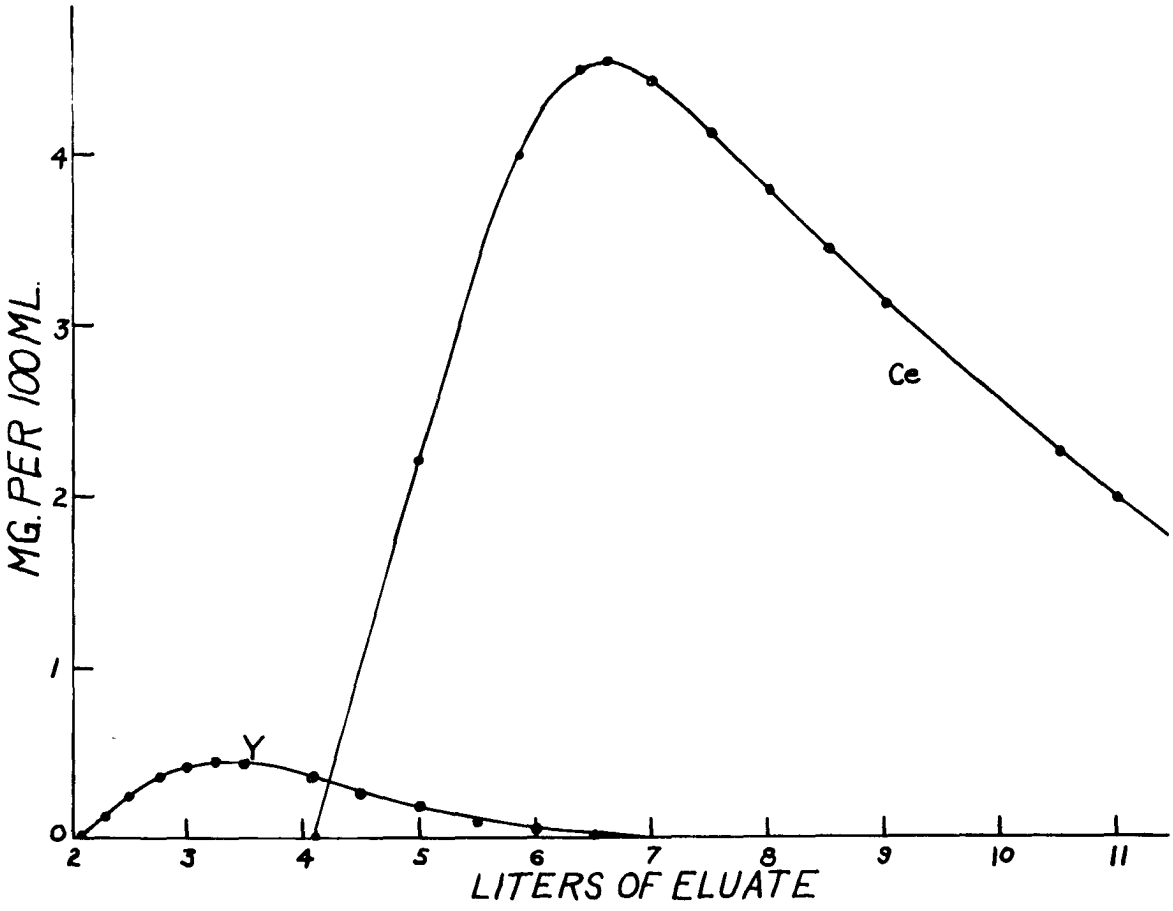

Figure 3. The elution of a small amount of Y in the presence of a large amount of Ce: pH 2.77; flow rate 5 cm/min; column dimensions 16 mm x 190 cm; composition of starting material, 10 mg. Y and 250 mg. Ce.

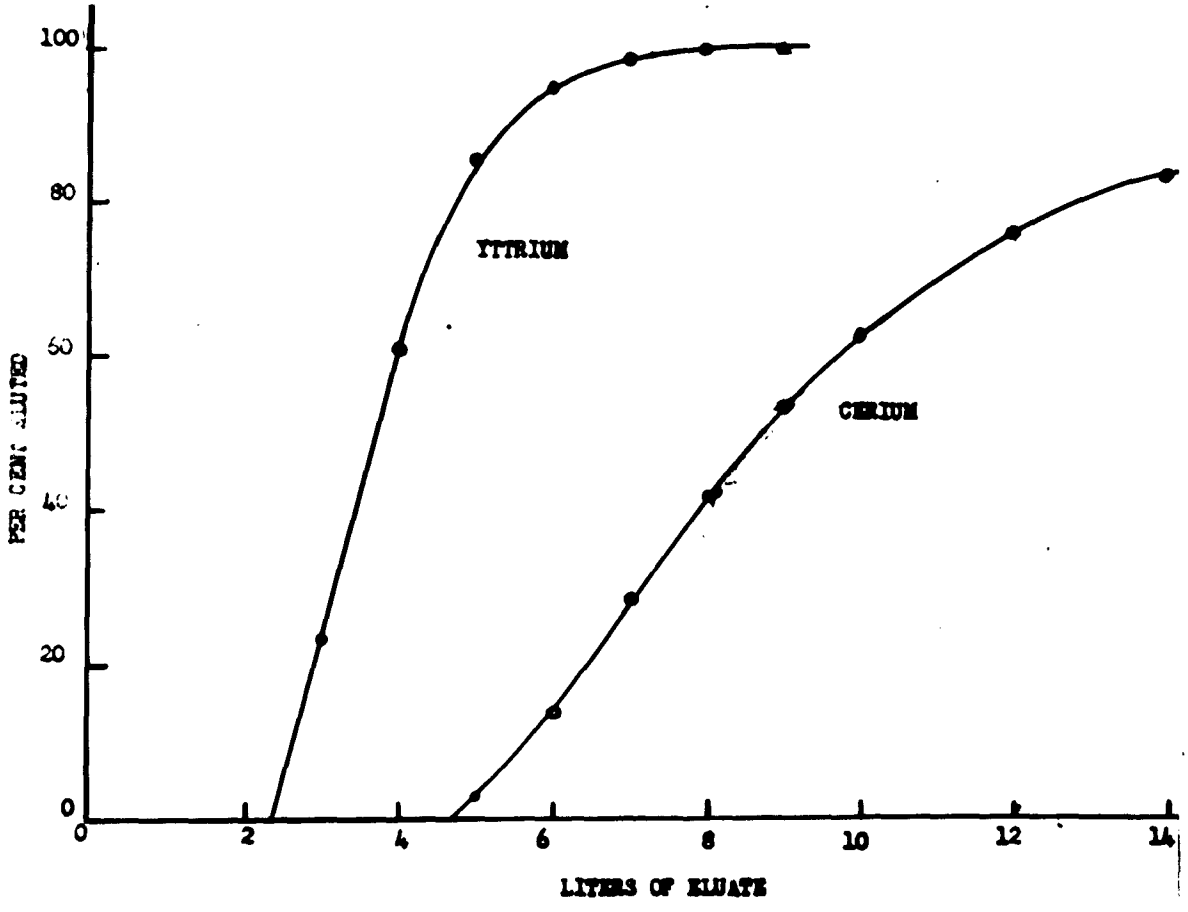

Figure 4. Separation of a small amount of Y from a large amount of Ce: pH 2.77; flow rate 5 cm./min.; column dimensions 16 mm. x 190 cm.; composition of the starting material, 10 mg. Y and 250 mg. Ce.

In this particular experiment, a 68% yield of pure yttrium and a 50-60% yield of pure cerium was obtained. The most important point concerning this experiment was the fact that the method actually separates trace amounts, leaving some of the major constituent of spectroscopic purity.

c) The effect of the column length. The optimum pH range of 2.60-2.66 was utilized in determining the extent of enhancing the separation of the cerium and yttrium elution bands from each other by resorting to much longer columns. It was shown in Part II of this section that cerium and yttrium are eluted at different rates under the same operating conditions. It might be expected that the band fronts would move farther apart as they progressed down the column, thereby making the process more efficient with longer columns.

A column was constructed having a diameter of 32 millimeters and a bed length of 600 centimeters. The pH of the eluant was 2.55 and the flow rate maintained at five centimeters per minute. The starting material consisted of 250 milligrams of cerium, 250 milligrams of yttrium, plus tracers of both elements. The positions of the activity peaks relative to each other were determined periodically during the course of the elution. The data so obtained is presented in Table 4, showing that the band maxima actually separated farther from each other as more eluant was passed

TABLE 4

SEPARATION BETWEEN THE TWO BAND MAXIMA OF Ce AND Y IN A 600 CM. COLUMN

Liters of Eluate	Separation in cm.
16	173 ± 15
20	193 ± 15
24	218 ± 15
28	236 ± 20
32	297 ± 20

through the column. The bands, in themselves, spread out over a large portion of the column, as was noted through the radioactivity measured with the portable G. M. Survey Meter. As a result, the separation of the two elements is not improved, due to the large degree of overlapping of the bands. Only 90-95% of the yttrium was free from cerium contamination. This apparently contradictory state of affairs can be caused by several factors: (1) the flow rate was too fast, which would lead to a process which is far from being operated as an equilibrium process, (2) straggling or tailing of the band, and (3) possible diffusion of the ions within the column. The conclusion should be drawn that beyond a certain critical length (to be determined by experiment) no improvement in separation can be gained by increasing the length of the column.

d) The effect of citrate concentration. Considering the results of the experiments using 5% and 20% citrate solutions in eluting tracer amounts of cerium and yttrium, the elution was repeated on macro amounts with a 2% citrate solution. However, this time the material on the column was not desorbed, but stayed on the top of the bed of resin. It was quite apparent, then, that the narrow pH range which has been used is adaptable only to 5% citrate eluant solutions. A calculation from the ionization constants of 5% citric acid shows that the concentration of the $(H_2Cit)^-$ ion reaches a maximum at pH of 3.2. A pH of 2.75 effectively controls the amount of this ion in solution and the ability of this ion to form stable complexes with the rare earth ion in solution. The conclusion can be made that for every citrate ion concentration, there will correspond a pH range which can be used to the greatest advantage in eluting the material. Because of this fact, all of the succeeding experiments to be described in this thesis were conducted with 5% citric acid as eluant.

e) Summary. The separation of cerium from yttrium with 5% citrate as the eluant is dependent upon the pH of the eluant. Table 2 shows the amount of yttrium eluted before the cerium breakthrough for each one of the experiments conducted over a pH range. As the pH is lowered, the point of breakthrough occurs at greater volumes of eluant and the

amount of eluant necessary to completely remove the yttrium is increased considerably. For the separation of yttrium from cerium, the 5% citrate is most efficient as an eluant when the pH is in the range 2.60-2.66. From the experiment using ten milligrams yttrium and 250 milligrams cerium, it can be concluded that if the best conditions are utilized for the separation of these elements, one can remove that element which is present in small amount in the starting material from the bulk of the remaining material. This suggests the employment of a series of columns so that the rich fractions from one column can be readsorbed and enriched further on a second column, ultimately leading to a pure product in two or three passes.

An important result of the experiments on column length is that an increase in the length of the column does not necessarily improve the yield of pure material. However, this may be the result of column operating conditions which are so remote from equilibrium conditions that the results can appear anomalous.

IV The Separation of Neodymium and Praseodymium

a) General considerations. The application of the ion-exchange process to the separation of rare earths in general makes the study of a neighboring pair of elements imperative. The choice of neodymium and praseodymium was made because of the availability of them. They are the principal components of didymium. Since their basicities are very close

to each other, and in view of the fact that only the trivalent states of their ions are known in solution, the selection of this pair will furnish a rigorous test of the applicability of the process.

In a preliminary experiment using a 16 millimeter column, bed length 150 centimeters, a flow rate of 6 centimeters per minute and the pH of the eluant of 2.75, it was shown that an enrichment of neodymium occurred in the front fractions eluted while the praseodymium concentrated in the tail fractions. The experiments which followed were systematically performed to improve the separation.

b) Effect of pH. In the experiments performed with yttrium and cerium, it was found that the pH range 2.60-2.66 gave the greatest amount of separation. This does not necessarily mean that the same pH range would give the best separation for all of the rare earths, but it is reasonable to believe that this pH range (2.60-2.66) would serve as an index for similar studies with neodymium and praseodymium. The pH region chosen for study extended from 2.53 to 2.76. The columns used were all 16 millimeters in diameter and had resin bed lengths of 160 centimeters. The flow rate of the eluant was maintained at 5-6 centimeters per minute.

(1) Experiments at pH 2.53 and 2.75. The weight of the samples used was 1.33 grams (as oxide). A spectrophotometric analysis of the starting material showed 21% Pr and 79% Nd. The results of the experiments are presented in

Table 5. A purity curve for the eluted neodymium is shown in Figure 5, obtained from data given in Table 7.

The two curves show conclusively that the lower pH value gives a better separation, not only for the production of pure neodymium, but also for preparing highly enriched samples in greater yield.

(2) Experiments at pH 2.55 and 2.65. The experiments described in paragraph (1) above were repeated, using the same columns and flow rates, but the pH values used were 2.55 and 2.65 and the starting material analyzed 43.4% Pr and 56.6% Nd. The total weight of starting material was one gram, calculated as oxide. The reason for using a starting sample with a higher praseodymium content was to increase the amount of praseodymium in the eluted samples so that the analysis could be conducted with greater accuracy. The data from the experiment is presented in Table 6 and the purity curves, drawn from the data in Table 7, are shown in Figure 6.

The pH experiments conducted here substantiate the results already presented in part II of this section. Also, it shows that the efficiency of the separation of neodymium from praseodymium is increased at a pH which is lower than the pH range considered best for cerium and yttrium. The possibility still exists that a further reduction in the pH of the eluant would increase the separation.

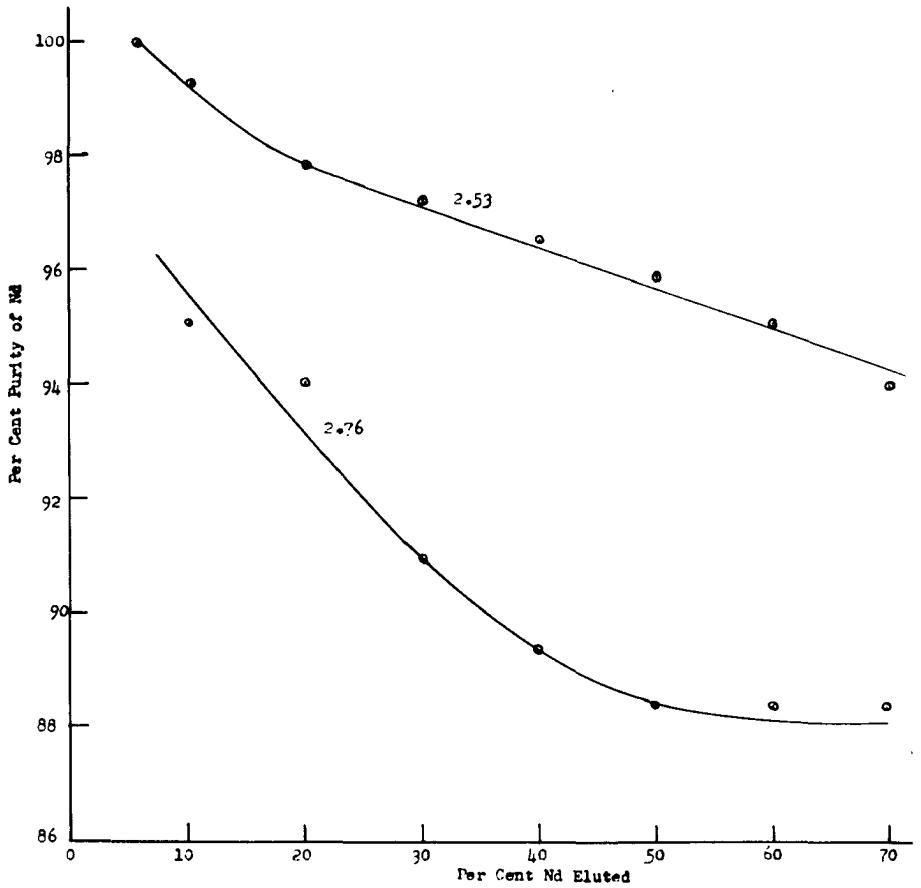

Figure 5. The effect of pH on the purity; column dimensions 16 mm. x 175 cm.; flow rate 5-6 cm./min.; composition of starting material, 79% Nd, 21% Pr.

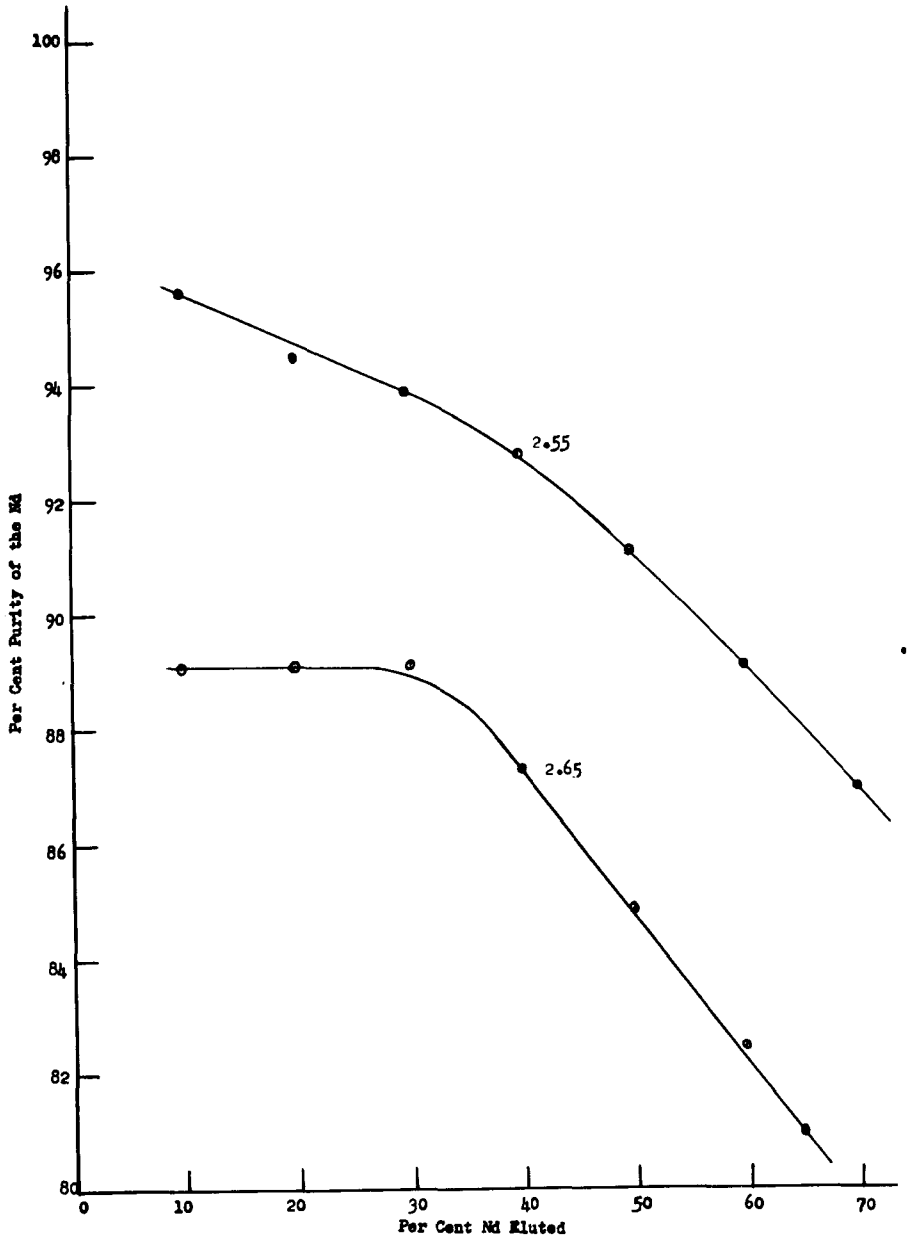

Figure 6. The effect of pH on the purity; column dimensions, 16 mm. x 175 cm.; flow rate, 5-6 cm./min.; composition of starting material 57% Nd and 43% Pr.

TABLE 5

THE EFFECT OF pH UPON THE SEPARATION OF Nd AND Pr

pH 2.75			pH 2.53		
	Per Cent Eluted			Per Cent Eluted	
Liters	Nd	Pr	Liters	Nd	Pr
3	4.5	--	8	0.5	--
4	36.4	14.4	9	4.0	0
5	66.5	37.7	10	11.5	0.7
6	82.0	54.6	11	21.6	1.9
7	89.5	66.8	12	32.4	3.8
8	92.5	75.0	13	42.7	6.2
9	94.4	80.8	14	52.0	9.0
10	95.7	85.0	15	60.6	12.0
11	96.7	88.3	16	67.5	15.8
12	97.0	90.0	17	73.5	19.4
13	97.5	91.3	18	78.3	23.4
			19	82.0	27.4
			20	85.0	31.2
			21	87.5	35.0

c) Weight of sample. If the rare earth samples are initially adsorbed on the Amberlite IR-1 in the acid cycle with the pH of the solution containing the rare earths at 1.8, then the amount of resin required for the adsorption is minimized. Also, the amount of exchanger necessary for

TABLE 6

THE EFFECT OF pH UPON THE SEPARATION OF Nd FROM Pr.

pH 2.65			pH 2.55		
	Per Cent Eluted			Per Cent Eluted	
Liters	Nd	Pr	Liters	Nd	Pr
4	5.4	0.5	9	17.0	1.3
5	41.6	8.1	10	38.0	3.8
6	73.0	23.5	11	55.0	8.0
7	89.5	39.1	12	67.6	12.6
8	97.6	51.5	13	77.0	18.1
9	101	61.0	14	83.8	23.5
10	103	68.0	15	88.8	29.0
11	104	73.5	16	92.5	34.5
12	105	77.5	17	95.5	39.0
			18	97.0	44.1

adsorption depends upon the valence state of the cation, the capacity of the resin, and the rate at which equilibrium is attained. Therefore, by adsorbing all trivalent rare earth samples at a pH of 1.8 and at the same rate the amount of resin required should be dependent upon the total amount of material adsorbed. It is assumed that the sample of mixed rare earths is adsorbed homogeneously, and that very little separation is effected in the adsorption process.

The experiments described herewith were performed to study the effect of the sample size upon the separation,

TABLE 7

DATA FOR PURITY CURVES OF Nd FROM pH EXPERIMENTS

% Nd Eluted	Original, 21% Pr, 79% Nd		Original, 43.4% Pr, 56.6% Nd	
	pH 2.53	pH 2.75	pH 2.55	pH 2.65
10	99.2	95.0	95.6	89.1
20	97.8	93.2	94.5	89.1
30	97.1	91.0	93.9	89.1
40	96.5	89.4	92.8	87.3
50	95.9	88.4	91.1	84.9
60	95.1	88.4	89.1	82.5
70	94.0	88.4	87.0	79.6
80	--	--	84.0	77.8
90	--	--	79.6	--

under a constant set of conditions. Several experiments were run in which the total bed length of the resin and the column diameter were held constant, while varying weights of starting material were employed. The object was to determine the maximum amount of material which could be adsorbed initially without adversely affecting the efficiency of the separation in the desorption step.

(1) Four columns were constructed, each having a diameter of 16 mm and a resin bed length between 160-170 cm. The pH of the eluant was adjusted to 2.66 with the elution carried out at a flow rate of six centimeters per minute on all the columns. The amounts of material used were 0.4765, 0.953, 1.906, and 3.812 grams of oxide. An analysis of the starting material, which was of the same composition on each column, showed 17% Pr and 83% Nd.

To determine the amount of the bed length which was used in the initial adsorption step, cerium activity was added to the starting sample. If the assumption is correct that there is no separation in the adsorption step, then the cerium activity will be interspersed homogeneously throughout that part of the resin which is used for adsorbing the sample. This can be measured quite accurately by measuring the activity through the glass wall of the column with the portable counting device. The results showed that the actual column length consumed in adsorbing the sample was directly proportional to the weight of the sample. The pertinent data obtained at the start of the experiments are given in Table 8.

Since the effective bed length available for separation during the desorption step was different in each case, the volume of eluant necessary for the breakthrough varied from one column to the next. Five liters were required for the 0.4765 gram sample while 2.8 liters were necessary for the breakthrough of the 3.812 gram sample. The overall elution curves were of the same general shape in each case, the differences lying in the concentration of the rare earth in the eluates which increased with the original sample size.

An analysis of the total elution curve and individual elution curves reveals the data presented in Tables 9 (a) and 9 (b). The data from Table 9 (b) are used in

TABLE 8

THE EFFECT OF WEIGHT OF SAMPLE ON THE SEPARATION OF Nd AND Pr

Column	Weight of Sample	Length of Column	Length Used in Adsorption Step	Effective Bed Length
1	0.4769 g.	178 cm.	7.5-9 cm.	~170 cm.
2	0.953 g.	173 cm.	19 cm.	~154 cm.
3	1.906 g.	168 cm.	36-38 cm.	~130 cm.
4	3.812 g.	168 cm.	68-71 cm.	~100 cm.

preparing the purity curves (Figure 7) for the separation. The purity curves show that for a given column size, there is a maximum amount of material which can be adsorbed initially without adversely affecting the separation. A comparison between the 0.476 gram and 0.953 gram samples shows very little difference in the separation. However, the results with the other two columns became increasingly poorer as the sample size became larger. This fact is only logical, since one must consider how much of the total bed length is used in adsorbing the material.

2) To firmly establish the fact that there exists an optimum weight of sample for each size column, four columns were erected, having sixteen millimeter diameters and bed lengths of 350 centimeters. The weights of the samples were nearly the same as those used in those experiments described in part (1) of this section. The flow rates were kept constant at six centimeters per minute, and

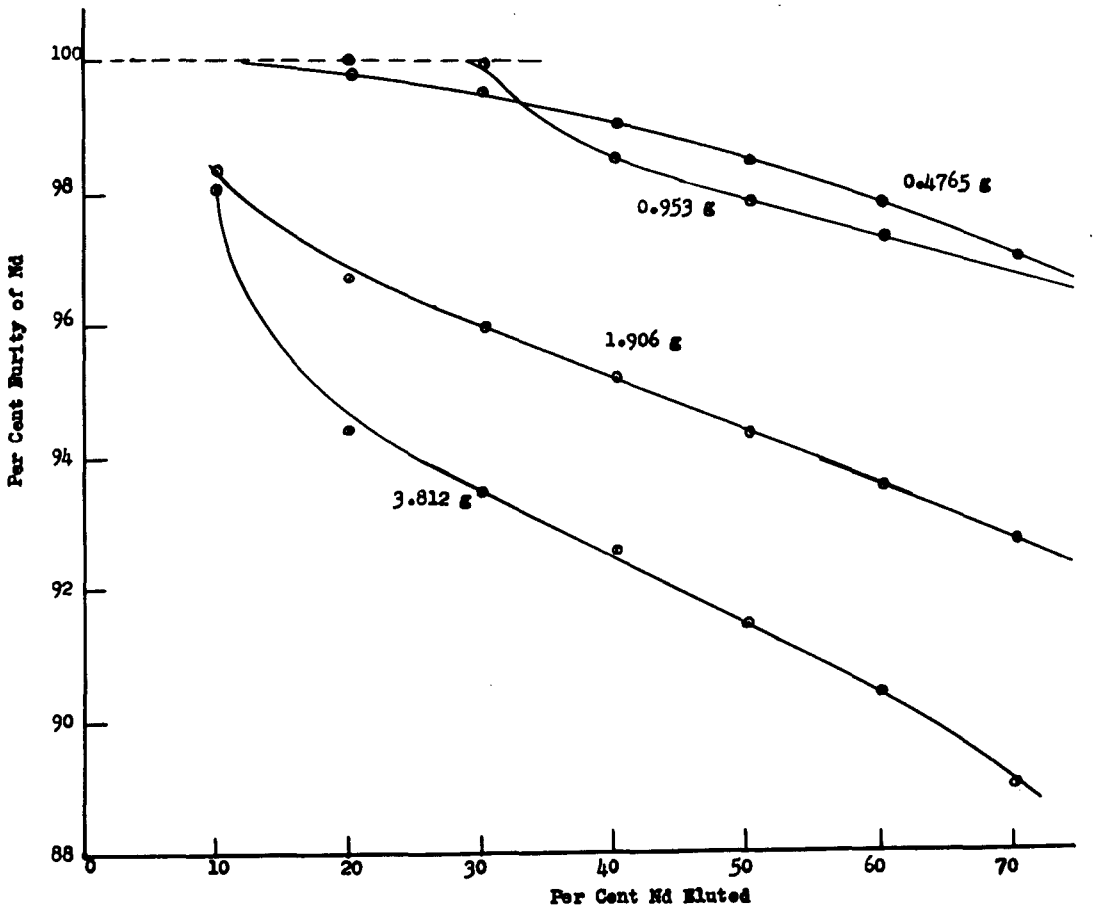

Figure 7. The effect of weight of sample on the separation; column dimensions, 16 mm. x 175 cm.; flow rate 6 cm./min.; pH 2.66; composition of starting material, 83% Nd with 17% Pr.

TABLE 9 (a)

SEPARATION DATA FOR WEIGHT OF SAMPLE EXPERIMENTS

	0.4765 g.		0.953 g.		1.906 g.		3.812 g.	
Liters	% Eluted Nd	Pr	% Eluted Nd	Pr	% Eluted Nd	Pr	% Eluted Nd	Pr
3	--	--	--	--	--	--	0.5	--
4	--	--	--	--	0.5	--	22.7	7.1
5	--	--	1.3	--	18.3	2.5	52.6	25.3
6	5	--	17.0	0.2	47.9	13.5	69.8	42.7
7	24	0.6	43.0	5.8	67.5	25.2	--	--
8	47.4	4.0	63.4	15.2	74.0	30.0	--	--
9	67.5	8.1	70.5	19.0	--	--	--	--

TABLE 9 (b)

PURITY DATA FOR WEIGHT OF SAMPLE EXPERIMENTS USING Nd AND Pr.

% Nd Eluted	0.4765 g. % Purity of the Nd	0.953 g. % Purity of the Nd	1.906 g. % Purity of the Nd	3.812 g. % Purity of the Nd
10	--	--	98.2	98.0
20	99.7	99.9	96.2	94.3
30	99.4	99.6	95.	93.4
40	98.9	98.4	95.1	92.5
50	98.4	97.8	94.3	91.4
60	97.8	97.3	93.5	90.4
70	96.9	96.9	92.7	89.0
80	--	96.1	--	--
% Pure Nd Eluted at Pr breakthrough	15.0	17.0	7.5	1.5

the pH of the influent citrate was 2.65. The starting material contained 43.4% Pr and 56.6% Nd. Cerium tracer was added to each of the samples to determine the length of the resin bed which was used in the adsorption step.

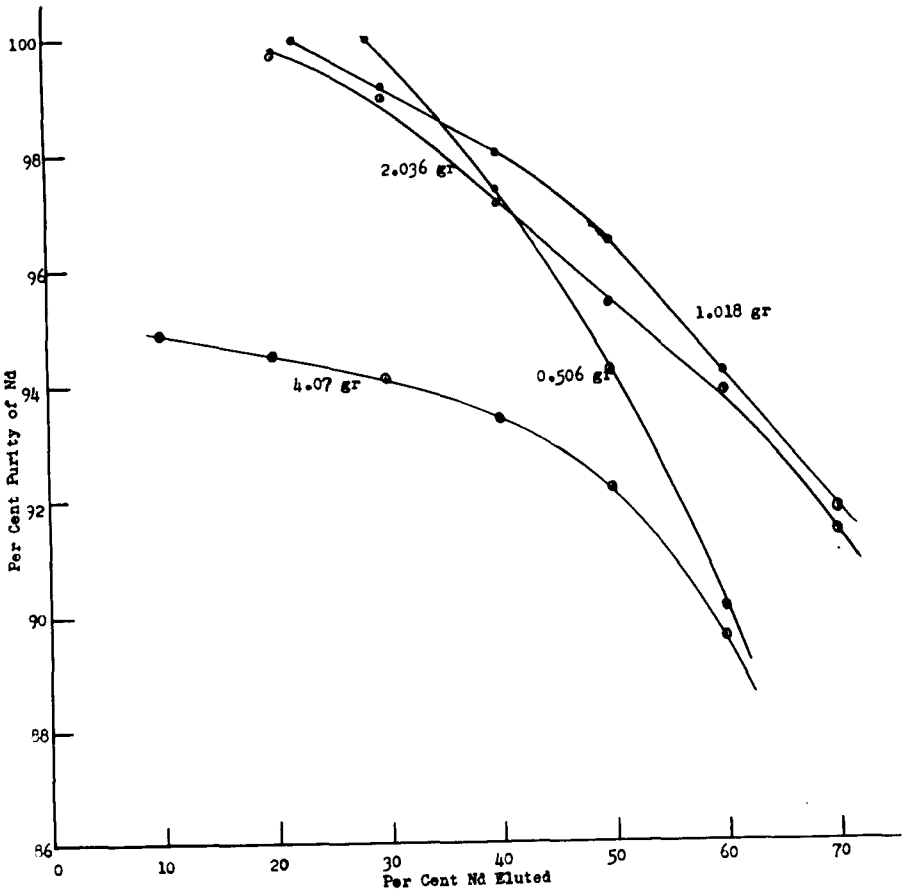

Figure 8. The change in separation with change in the weight of sample using longer columns; column dimensions, 16 mm. x 350 cm.; flow rate, 6 cm./min.; pH 2.66; composition of starting material, 56.6% Nd with 43.4% Pr.

The straight lines of the principal part of the curves are represented in Table II. The effective bed lengths were determined by subtracting the length of column used for separation from the total length of the column. The breakthrough curves given in Fig. 11 (a) and 11 (b). The results obtained are helpful for calculating the concentration of rare earths per liter of the original solution and the results also very accurate determination. It is found that the breakthrough for this column did occur until 11.4 liters of eluent, which is far beyond what one would expect from a calculation of the free void volume of the ion exchanger. This fact, and the low concentration of rare earth in the eluate show that the material on the column moving very slowly over the entire column during the course of the separation, and that considerable overlapping of the individual elutions occurs.

Table II

EFFECT OF [illegible] ON THE [illegible]

Column	Wt. of Resin, Grams	Total Bed Length, C.M.	Effective Bed Length, C.M.	Breakthrough, Liters	Conc. of Eluting Acid, gm/l
1	3.603	361	343	22.5	93
2	1.316	354	330	14.1	97
3	2.036	363	319	11.7	109
4	4.372	344	174	7.0	4.

Referring to Figure 8, one can see that the separation with the 1.018 gram sample is of the same order of magnitude as that with the 0.509 gram sample, within experimental error. These separations are both better than the corresponding experiments described in part (1) with the 175 centimeter columns, in spite of the fact that the starting material was, in the present case, richer in praseodymium. Approximately 22.5% of the neodymium eluted was 100% pure with the 1.018 gram sample as compared with only 4% of the neodymium prepared pure with the column which contained 2.036 grams of material.

Considering the results presented in parts (1) and (2) of this section, one can safely conclude that there is a certain weight of sample for a given column size which will afford the same relative amount of pure material as will a smaller starting sample of the same material. Increasing the sample size beyond this weight materially reduces the degree of the separation.

d) Effect of column length. It was very desirable to know if a change in the length of the column would have any effect upon the separation of neodymium from praseodymium. It was illustrated with cerium and yttrium that the degree of separation did not increase when the column length was increased from 175 centimeters to 810 centimeters at the low pH of 2.55, even though the peaks did progressively move farther apart. In order to make a direct measurement of the

TABLE 11 (a)

SEPARATION DATA FROM WEIGHT OF SAMPLE EXPERIMENTS
USING ~350 CM. COLUMNS

0.509 g.			1.018 g.			2.036 g.			4.072 g.		
Liters Eluate	% Eluted Nd	Pr	Liters Eluate	% Eluted Nd	Pr	Liters Eluate	% Eluted Nd	Pr	Liters Eluate	% Eluted Nd	Pr
24	2.6	--	16	1.9	--	12	0.2	--	11	3.6	0.1
25	7.4	--	17	12.0	--	13	4.1	--	12	19.1	1.1
26	13.3	--	18	21.0	0.1	14	17.0	0.1	13	38.6	3.6
27	20.5	--	19	34.0	0.45	15	33.2	1.1	14	54.5	7.0
28	28.2	0.1	20	46.0	1.0	16	48.1	2.6	15	65.0	11.4
29	35.5	0.6	21	56.3	1.9	17	60.2	5.1	16	73.2	16.5
30	40.5	1.6	22	64.8	3.0	18	69.5	8.3	17	79.9	21.5
31	46.5	3.0	23	71.7	4.8	19	76.1	11.6	18	84.5	26.5
32	50.5	4.4	24	77.0	7.1	--	--	--	19	87.5	31.6
33	55.4	6.1	25	81.0	10.0	--	--	--	20	89.8	36.0
34	59.2	8.1									
35	62.6	10.1									

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TABLE 11 (b)

EFFECT OF SAMPLE SIZE ON THE ELUTION
FROM A ~350 CM. COLUMN

% Nd Eluted	0.509 g. % Purity Nd	1.018 g. % Purity Nd	2.036 g. % Purity Nd	4.072 g. % Purity Nd
10	--	--	--	94.9
20	--	--	99.7	94.5
30	--	99.1	98.0	94.1
40	97.4	98.0	97.1	93.4
50	94.2	96.5	95.4	92.2
60	90.1	94.2	93.9	89.8
70	--	91.9	91.5	86.6
80	--	--	--	82.8
90	--	--	--	76.6
% Nd Eluted at point of Pr breakthrough	29.0	22.5	4.0	40

effect of column length, samples of identical composition and size were used on columns of varying lengths.

(1) A one gram sample of a neodymium-praseodymium mixture containing 43.4% praseodymium was adsorbed on a 16 millimeter column having a bed length of 175 centimeters. Desorption was carried out with pH of 2.65 at a flow rate of six centimeters per minute. These are precisely the same conditions which were employed in the experiment

described in part (2) of the preceding section using a 350 centimeter column. The elution data for the sample on the 175 centimeter column are given in the first three columns of Table 12. The purity data for the 350 centimeter column experiment (column 6 in Table 12) were taken from the weight of sample experiments presented in column 3 of Table 11 (b). Utilizing these data, the purity curves for each of these experiments are shown in Figure 9. The purity curves show that the separation of neodymium from praseodymium is markedly improved by an increase in the resin bed length.

(2) Data obtained from experiments using columns with 49 millimeter diameters substantiate the results above. These results are listed in the last two columns of Table 12. One column was 175 centimeters long and had nine grams of material adsorbed on it. The other column had a bed length of 728 centimeters and used 48.8 grams of material. Both columns were operated at a pH of 2.65 and with a flow rate of five centimeters per minute. The starting material was the commercial didymium which has been described as containing 78% Nd, 18% Pr and 2.5% Sm.

While there are two variables which are not being held constant in this set of experiments (column length and sample size), one can obtain pertinent information concerning the separation. In the case of the 175 centimeter column, the ratio of grams of adsorbed material per centimeter of resin bed is 0.00514 while with the 728 centimeter column, the

TABLE 12

EFFECT OF COLUMN LENGTH ON THE SEPARATION OF Nd AND Pr

Liters Eluant	175 cm. % Nd	175 cm. % Pr	% Nd Eluted	% Purity of Eluted Nd 175 cm.	350 cm.	175 cm.	728 cm.
4	5.4	0.4	10	89.1	--	98.6	99.8
5	41.6	8.2	20	89.1	--	98.2	99.5
6	73.4	23.5	30	89.0	99.1	97.4	99.1
7	89.6	39.0	40	87.3	98.0	96.4	98.6
8	97.6	51.5	50	85.1	96.5	95.4	97.9
9	101.0	61.0	60	82.7	94.2	94.1	97.0
10	103.0	68.0	70	79.5	91.9	92.6	95.7
11	104.0	73.0	80	77.8	--	91.8	93.8
12	105.0	77.5	90				
% Nd Eluted at Pr Breakthrough				3.5	22.5	1.5	5.0

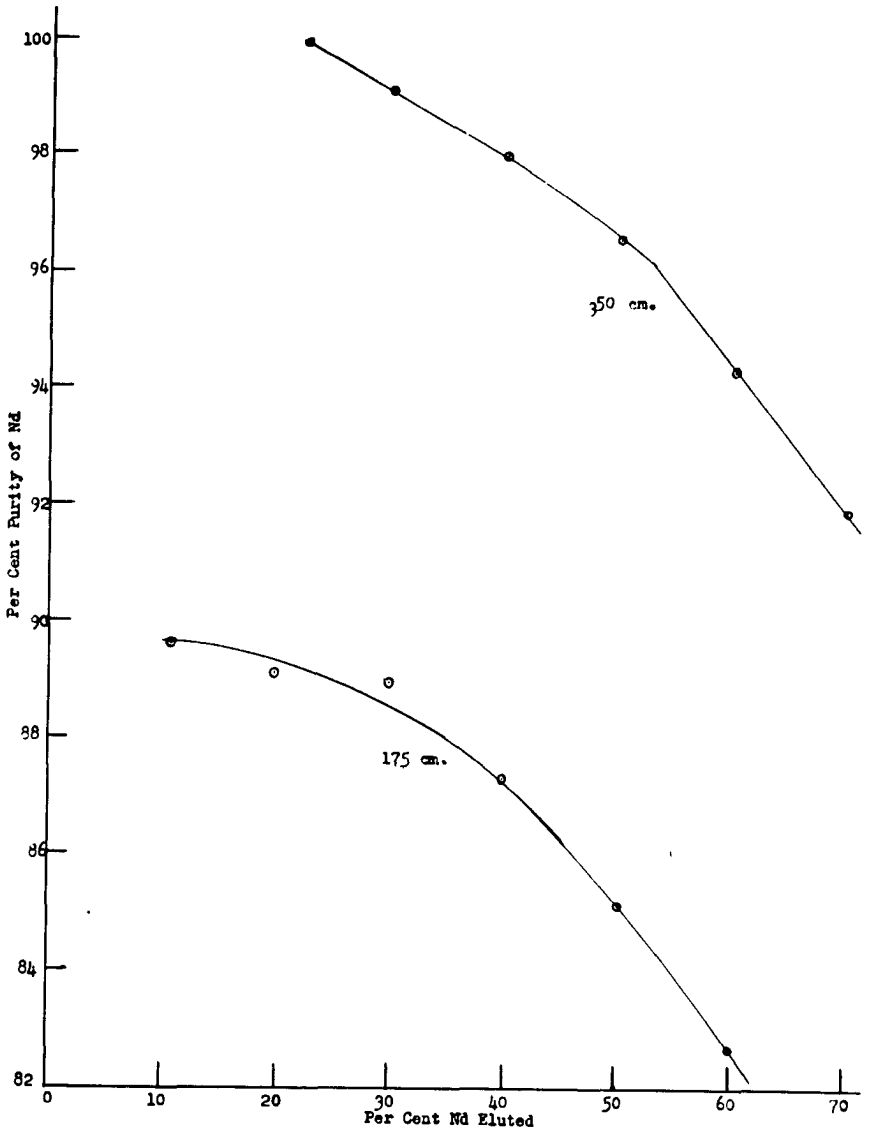

Figure 9. The effect of column length on the purity: pH 2.65; flow rate 6 cm./min.; column dimensions, 16 mm. x 175 cm. and 16 mm. x 350 cm.; composition of starting material 56.6% Nd and 43.4% Pr; weight of sample, 0.5 gr./cm.^{2}

ratio is 0.00574. If the length of column were not a factor, these facts would predict that the shorter column (the 175 centimeter column in this case) would give the better separation.

The purity curves which were drawn from the data in columns 7 and 8 of Table 12 are shown in Figure 10. These curves further substantiate the belief that the separation is better for the longer column. By comparing columns 5 and 6 with columns 7 and 8 in Table 12, it is seen that the increase in separation is more marked when the weight of sample is held constant and the column length increased, than when the weight of sample per centimeter of effective bed length is kept constant. The discrepancies between the results in columns 5 and 7 are, for the most part, due to the differences in the neodymium to praseodymium ratio in the starting material. The effect of differences in composition of the starting samples on the separation will be discussed more fully in a later section.

e) The effect of flow rate. Since the separation of one rare earth from another in the course of the elution depends upon the relative number of times that the ions exchange with the resin as it is eluted through the column, the maximum efficiency is obtained when the difference is greatest. Such a state of affairs would entail operating the column under equilibrium conditions. Too fast a flow

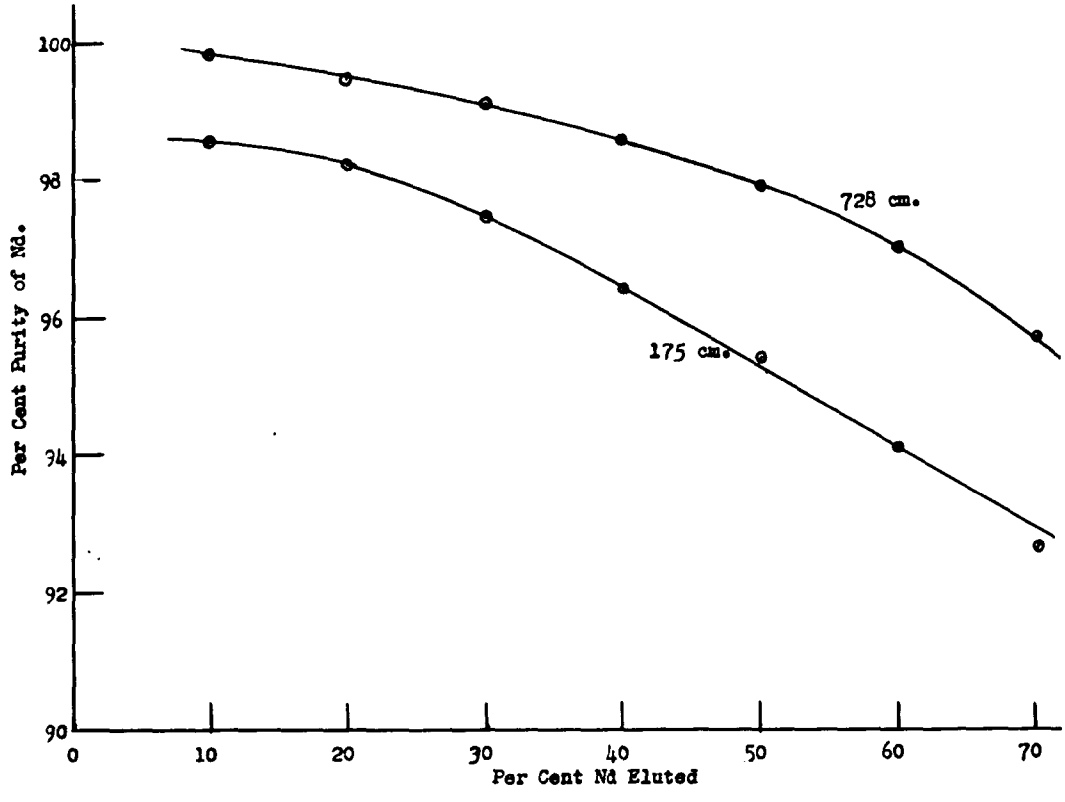

Figure 10. The effect of column length on the purity: column dimensions, 49 mm. x 175 cm. and 49 mm. x 728 cm.; pH 2.65; flow rate, 5 cm./min.; weight of starting samples; 0.5 gr./cm.^{2} on the 175 cm. column, 2.5 gr./cm.^{2} on the 728 cm. column; composition of starting material, 78% Nd, 18% Pr, and 2.5% Sm.

would upset the equilibrium and not allow for maximum efficiency. As the flow rate is reduced so that equilibrium conditions are approached, the ions in solution could diffuse back up the column and hence lead to no separation at all. Therefore a number of experiments were performed in order to determine an optimum flow rate for the separation.

Three columns were prepared having 16 millimeter diameters and bed lengths of 175 centimeters. The size of the sample used on each column was the same (0.953 grams of oxide), the elution being conducted at a pH of 2.65. The original samples analyzed 83% Nd and 17% Pr. The flow rates used were 3, 6, and 12 centimeters per minute, with the flow rate used for each column being held constant.

The breakthrough occurred in all cases between 3.5 and 4.0 liters. From the total elution curves as shown in Figure 11 it is readily seen that the concentrations of total rare earth at the elution peaks differ greatly from one column to the next. The concentration at the elution peak increases as the flow rate decreases; namely 3 centimeters per minute gives 372 milligrams per liter; 6 centimeters per minute, 246 milligrams per liter; and 12 centimeters per minute, 182 milligrams per liter. The data obtained from the total elution curves and individual elution curves are presented in Tables 13 (a) and 13 (b).

The curves showing the per cent of the total neodymium and praseodymium eluted as a function of the volume

of eluant are shown in Figure 12. A careful analysis of the data shows that the elution curves of the praseodymium are almost super-imposable, one on the other, if allowances are made for small differences in the actual breakthrough volume. The difference in separation was obtained at slower flow rates because the neodymium was eluted more rapidly, after once breaking through. This means that the neodymium band on the column became more sharply defined as the flow rate was decreased. The purity curves for the material on each column are presented in Figure 13.

The means by which the slower flow rates enhance the separation comes as a result of eluting the neodymium more efficiently. Slower flow rates would increase the number of times that an ion exchanges with the resin in the column. It appears plausible that the process becomes much more competitive at concentrations in the front part of the band, and so eliminates the appearance of the praseodymium. This means that the column is being operated at near equilibrium conditions at the slower flow rates, and hence it can be concluded that slower flow rates will enhance the separation until such a time when the process of back-diffusion becomes important. The time element becomes important as the decrease in flow rate increases the time necessary for an experiment, inasmuch as the breakthrough volume appears to be independent of the flow rate.

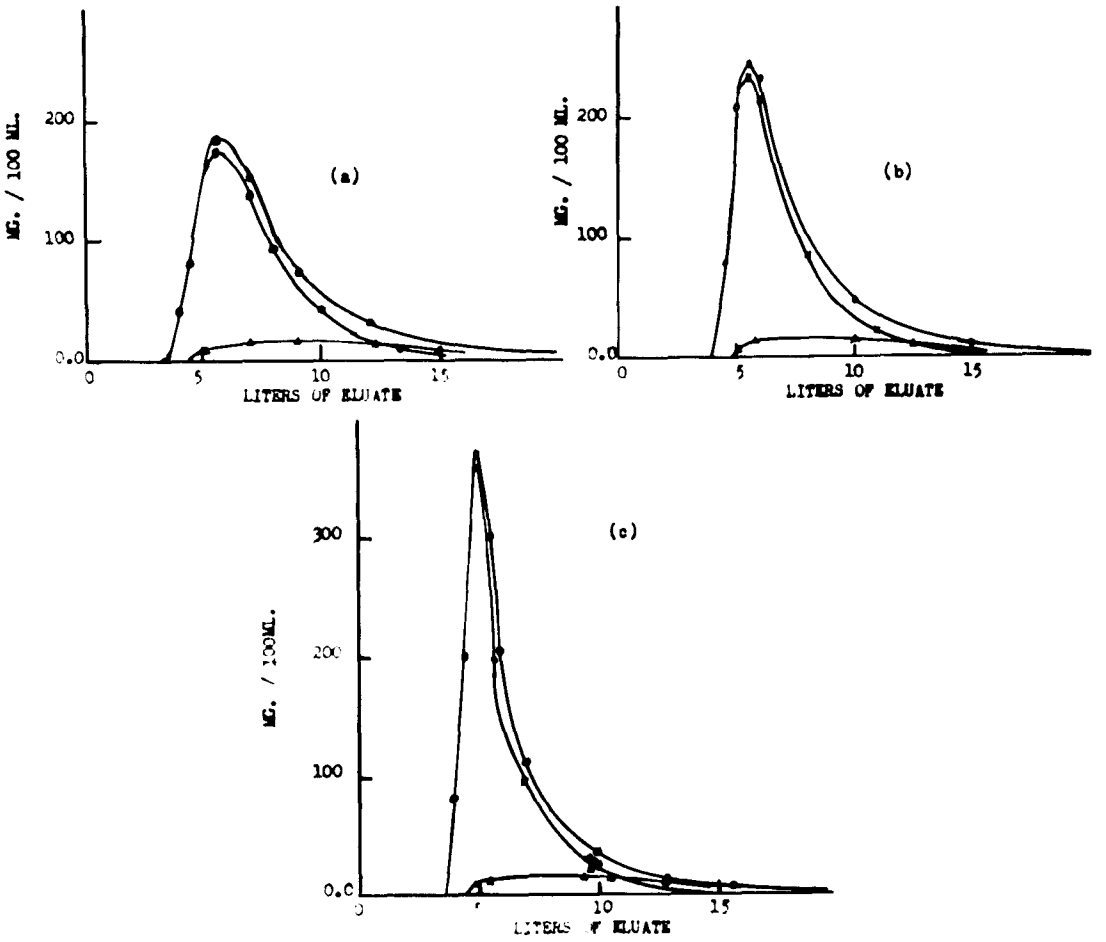

Figure 11. The elution curves of Nd and Pr using different flow rates: column dimensions, 16 mm. x 175 cm.; pH 2.65; sample weight, 0.476 gr./cm.^{2}; composition of starting material, 83% Nd and 17% Pr. Flow rates: (a) 12 cm./min.; (b) 6 cm./min.; (c) 3 cm./min. Top curve in each case represents the total weight curve, the intermediate curve the elution of Nd, while the lowest curve in each case represents the elution of Pr.

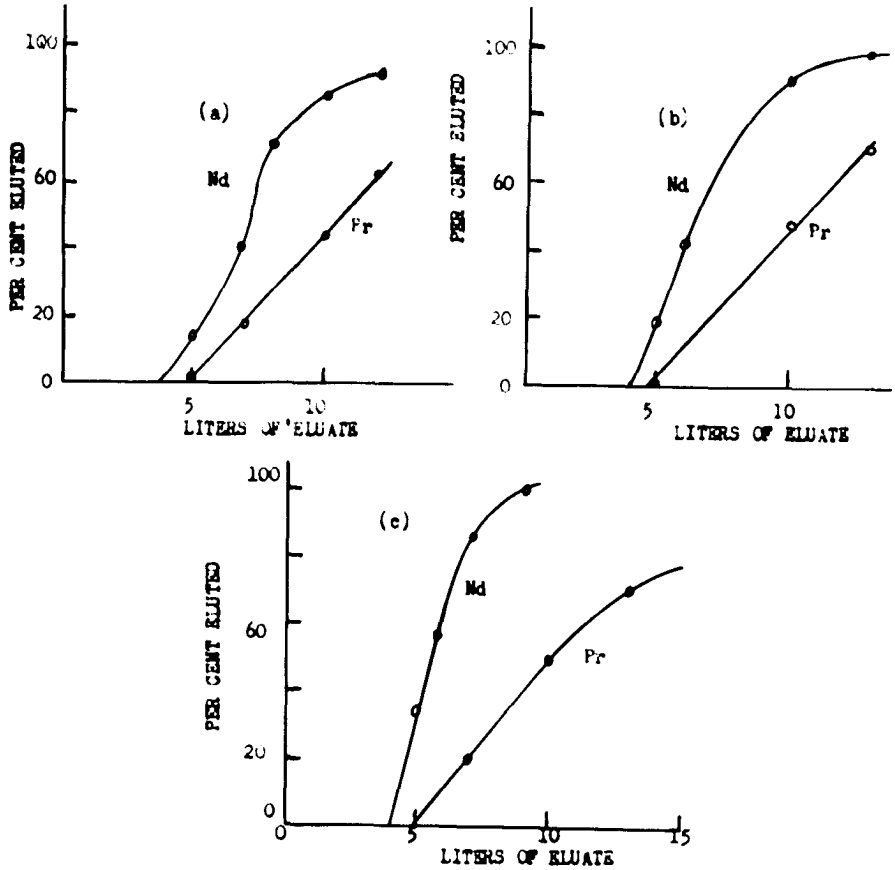

Figure 12. The separation curves of Nd and Pr using different flow rates: column dimensions, 16 mm. x 175 cm.; pH 2.65; sample weight 0.476 gr./cm.^{2}; composition of starting material, 83% Nd and 17% Pr. Flow rate: (a) 12 cm./min.; (b) 6 cm./min.; (c) 3 cm./min.

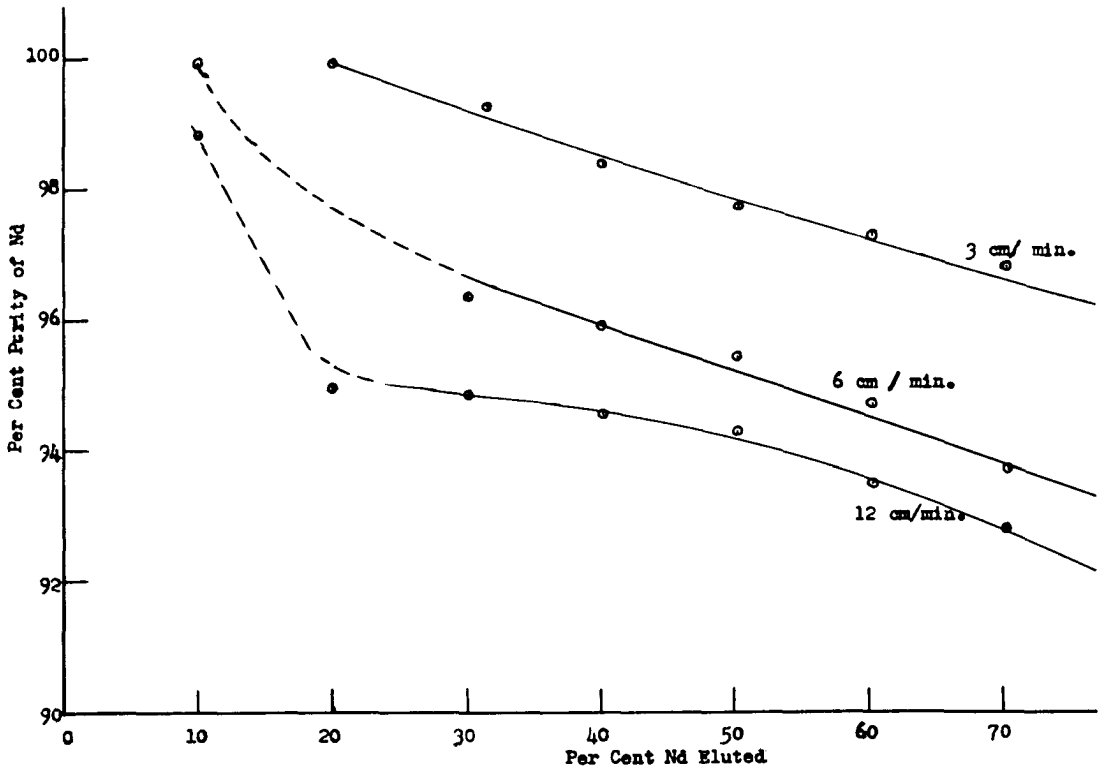

Figure 13. Purity curves showing the effect of flow rate on the separation: column dimensions, 2 16 mm. x 175 cm.; pH 2.65; sample weight, 0.476 gr./cm.

TABLE 13 (a)

EFFECT OF FLOW RATE ON THE SEPARATION OF Nd AND Pr

Liters	3 cm./min.		6 cm./min.		12 cm./min.	
	% Nd	% Pr	% Nd	% Pr	% Nd	% Pr
4	1.4	--	--	--	1.5	--
5	35.0	1.7	13.5	--	13.8	1.6
6	69.6	10.4	42.0	8.4	35.0	8.8
7	86.3	20.0	64.5	18.5	54.8	17.4
8	95.0	29.5	78.5	28.5	69.5	26.2
9	100.0	39.5	87.0	38.4	78.5	34.6
10	103.0	49.5	92.4	47.5	85.6	43.9
11	105.0	59.0	95.6	56.4	90.2	52.9
12	106.6	65.4	98.0	64.0	93.0	61.9
13	107.5	70.0	99.0	71.0	94.8	69.5
14	107.9	74.0	100.0	77.0	96.0	75.6
15	108.2	77.0	100.4	81.5	96.8	80.6

f) The effect of column diameter. The primary purpose in investigating the effect of the column diameter was to see if large diameter columns are feasible. The elution process is essentially an adsorption-desorption process which, for each ion, occurs many times during the course of progress through the column. When the average number of adsorption-desorption cycles for one ion species differs appreciably

from that of another species in a given length of column, a separation is effected. Particular care must be exercised in maintaining a definite band front as the material is eluted down the column. It has been stated previously that the efficiency of the separation is dependent upon working close to equilibrium conditions of flow rate as in this manner the band front for each ion species in the mixture is best defined.

TABLE 13 (b)

EFFECT OF FLOW RATE ON THE PURITY OF ELUTED SAMPLES OF Nd AND Pr

% Nd Eluted	% Purity of the Nd		
	3 cm./min.	6 cm./min.	12 cm./min.
10	--	100	98.9
20	100	97.4	95.0
30	99.6	96.4	94.9
40	98.4	96.0	94.6
50	97.8	95.5	94.4
60	97.4	94.8	93.6
70	96.9	93.8	92.9
80	96.1	92.9	91.9
% Nd Eluted at Pr Breakthrough	25.0	12.5	7.0

When larger columns are used, a certain amount of channeling occurs, with the result that the separation becomes impaired. In section (c), above, it was pointed out that above a certain weight of sample the separation is governed by the amount of adsorbed material. Expressing this in another way, the separation depends upon the proportionate amount of the column which is necessary to adsorb the material. Proceeding on this premise, one should expect to obtain the same degree of separation with larger diameter columns, each having the same bed length, if the amounts of rare earths used are in the ratio of the cross-sectional areas of the columns in which they are used, providing all other factors are held constant.

Four columns were constructed, each having a bed length of 175 centimeters, the diameters being 16, 32, 49, and 64 millimeters. The weights used were 1, 4, 9, and 16 grams respectively. The starting material contained 20% Pr and 80% Nd. The weights correspond to 0.5 grams per square centimeter of cross-sectional bed area. The flow rates were held constant at 6 centimeters per minute, and the pH of the citrate was 2.65.

The elution data obtained after analysis of the samples are given in Tables 14 (a) and 14 (b). The results tabulated in Table 14 (b) are presented graphically in Figure 14. The purity curves show that changing the column diameter has made little difference in the

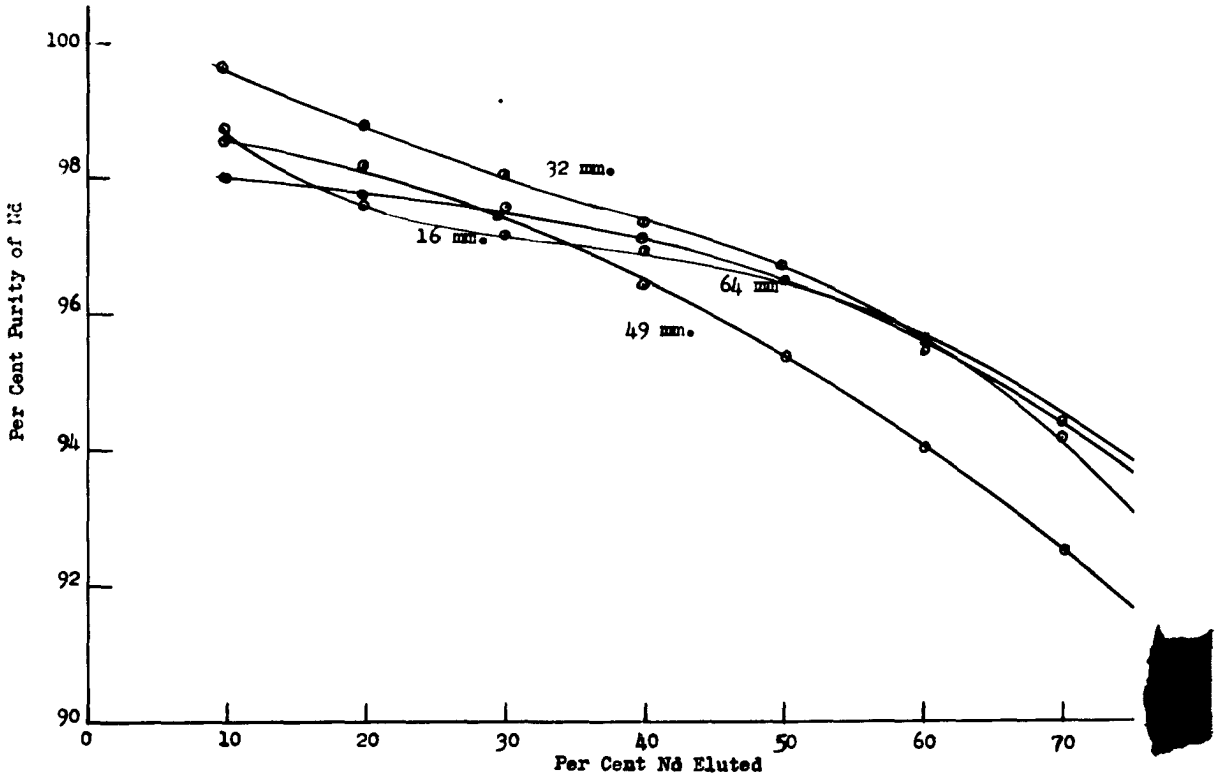

Figure 14. The effect of column diameter on the separation of Nd and Pr: column length 175 cm.; composition of starting material, 80% Nd and 20% Pr; weight of sample, 0.50 gr./cm.^{2}; flow rate, 6 cm./min.

TABLE 14 (a)

SEPARATION OF Nd AND Pr ON COLUMNS OF DIFFERENT DIAMETER

16 mm.			32 mm.			49 mm.			64 mm.		
Liters	% Nd	% Pr	Liters	% Nd	% Pr	Liters	% Nd	% Pr	Liters	% Nd	% Pr
5	12.0	0.7	20	0.1	--	50	0.1	--	100	2.1	--
6	42.0	10.6	24	5.4	0.1	58	4.1	0.1	110	7.5	0.5
7	65.5	18.8	28	24.1	1.5	66	16.1	1.3	120	15.8	1.6
8	79.1	23.5	32	45.3	5.4	74	31.9	3.7	130	27.1	3.0
8.5	83.3	28.3	36	60.2	11.2	82	45.4	8.0	140	39.2	4.6
			40	71.0	18.2	90	56.4	13.5	150	48.8	7.1
			44	78.4	25.9	98	65.6	19.1	170	63.9	12.9
			48	83.5	33.3	106	72.5	24.5	190	74.0	19.1
			52	86.8	39.8	114	77.9	29.7	210	81.1	25.8

TABLE 14 (b)

PURITY DATA FROM COLUMN DIAMETER EXPERIMENTS

	% Purity of the Eluted Nd			
% Nd Eluted	16 mm.	32 mm.	49 mm.	64 mm.
10	98.7	99.6	98.6	98.0
20	97.6	98.8	98.2	97.7
30	97.1	98.0	97.5	97.5
40	96.9	97.3	96.4	97.1
50	96.3	96.7	95.3	96.5
60	95.4	95.6	94.0	95.6
70	94.6	94.1	92.5	94.4
80	93.0	92.0	90.8	92.8

separation. The slight discrepancies in the figure are well within experimental error. Columns of 175 centimeters in length and large diameter can be considered practical, and should prove to be very useful in making crude or first cycle separations using large amounts of material.

g) Composition of the starting material. An important factor in obtaining a quantity of pure material in one pass through a column is the relative amounts of the components in the starting material. Since in any experiment the eluted material contains increasing amounts of the slower moving species, not much can be done to control its effect upon the elution. It is certain, however, that the total amount of pure material obtained in any one experiment is governed by the composition of the starting material. A brief discussion of this variable as applied to some experiments already described will serve to illustrate the degree to which this variable exerts itself.

(1) In the experiments at various pH values described in part (b), one column had a starting sample containing 21% Pr and was operated at a pH of 2.53. Another column, operating at a pH of 2.55, had a starting sample containing 43.4% Pr. The slight difference in the pH values, viz. 0.02 pH units, is not sufficient in magnitude to cause any large increase in the separation by itself. A

comparison of the two sets of curves in Figures 5 and 6 shows a large difference between them. From these figures, it is seen that the separation at pH 2.75 using 21% Pr, 79% Nd as the starting material is just as good as pH 2.55 with a sample which contains 43.4% Pr and 56.6% Nd.

(2) In making a comparison between the results in the weight of sample experiments when the same weights of material were used (see part (c) above), the data obtained therefrom could not be used in the length of column experiments (part (d) above). This was due to the fact that there was a large difference in the Pr/Nd ratio in the starting materials used in each length of column. With the 175 centimeter column, the starting material analyzed 17% Pr, 83% Nd, while with the 350 centimeter columns it was 43.4% Pr, 56.6% Nd. A comparison of the data in Table 9 (b) with the data in Table 11 (b) shows that the separation is as good with the 175 centimeter column as with the longer column for each sample weight. The conclusion was reached in part (d), above, that the separation improves with an increase in column length, so that the apparently anomalous results being discussed here can only be ascribed to the differences in the composition of the starting materials.

h) Considerations of the effects of other variables. There are several other factors that will affect the separation

which are not very important individually, but nevertheless must be considered. These include (1) the mesh size of the resin, and (2) the pH of the rare earth solution in the initial adsorption step. The experimental work connected with these factors was conducted at Oak Ridge (49, 57). It is shown that the smaller the mesh size of the resin, the better will be the separation. In the course of performing the experiments described in this thesis, the degree of packing of the resin in the column, when 100 mesh size resin is used, is such as to lower the flow rate to the point where there is practically no flow of eluant. While Boyd reported good operation of his columns, it must be stated that the columns in use here are much longer than those in use at Oak Ridge. The additional resin weight and liquid head forces the fine particles into the small interstices and effectively blocks the column to liquid flow. The 40-60 mesh resin size that is being employed in the experiments herein described was chosen because it was as fine as could be used without deleterious effects.

The pH of the initial rare earth solution should be in the range 1.6-2.5. If the pH is outside this range to any large extent, the amount of resin required to adsorb the sample becomes greater, which in turn lowers the efficiency of the column. One must be careful that the non rare earth salt concentration is not very high. If one dissolves the sample in a large excess of strong acid, then

the salt formed in adjusting the pH to, say, 1.8 is strong enough to partially elute the rare earths down the column a short distance. It is for this reason that the oxide material is dissolved in only a slight calculated excess of acid.

RESULTS

I The Establishment of a Standard Set of Conditions

From the foregoing data, it is possible to establish a set of standard conditions for the separation of the rare earths by elution. It must be realized that this set of conditions has been worked out for the separation of Nd and Pr, which are neighboring elements. It has been mentioned previously that the position of the element in the elution series depends upon the basicity of that ion. Some of the other rare earths have basicities which lie much closer to each other than do Nd and Pr. Then too, yttrium interposes itself into the actual rare earth group with the result that the efficiency of the separation under the conditions which appear to be best for neodymium and praseodymium may be quite different for the other rare earths. It is hoped, however, that this set of conditions may serve as a good starting point for further research.

One factor which has been mentioned, but not adequately emphasized, is the time necessary to perform a complete elution. It has been shown that the separation increases greatly with a decrease in the pH and in the flow rate, and an increase in the length of the column. However, to increase the column length by a factor of two would essentially increase the length of time necessary for the elution by at least a similar factor. The decrease in the flow rate

by one-half likewise increases the time factor by two. For the time being, let us assume that the column length is held constant at 175 centimeters.

At the start of this investigation, the assumption was made that all of the effects produced by the various factors are additive. Therefore, if the value for each variable is adopted which gives the best separation (other things being held constant) and applied to the elution of a sample, the separation obtained would represent the best separation possible for this particular pair of elements. These are presented in summary form:

a) pH. The best pH value for separating neodymium and praseodymium using 5% citrate lies between 2.50 and 2.55. Lower values would retard the elution to such an extent that any increase in the separation would be small and more than offset by the increase in the time necessary to elute the material. In the case of cerium and yttrium, an optimum pH value was found, below which the separation decreased.

b) Weight of sample. The maximum weight of material to be used on 175 centimeter columns is 0.5 grams of rare earth oxide per square centimeter of cross-sectional area. Actually, a value of between 0.25 and 0.50 grams per square centimeter is more advisable. If the length of the column is increased the weight of the starting sample can be increased

too, but not quite in direct proportion. This fact is borne out after examining the purity curves in Figure 8.

c) Flow rates. It was found that the separation increased on reducing the flow rate from 12 to 6 to 3 centimeters per minute. An additional increase in the separation may be attained if the flow rate is further reduced. At flow rates below 1 centimeter per minute, it becomes increasingly difficult to keep the flow adjusted to a constant rate when small diameter columns (16 millimeters or less) are being used. Then too, the possibility of back diffusion of the rare earth ions in solution increases as the flow rate decreases. It must be stated that back-diffusion has not been observed in any of the experiments conducted during the course of this work.

d) Diameter of the column. To date, the largest diameter column used had a 4 inch diameter. If the resin bed is properly backwashed and conditioned the differences in separation from one diameter column to another are so slight as to be within experimental error.

An experiment was performed to test this particular set of conditions. A 64 millimeter diameter column with a bed length of 175 centimeters was used. The resin was dry seived to 40-60 mesh size and backwashed and conditioned repeatedly. The sample used was 8.0 grams (0.25 grams per square centimeter) of oxide, containing 51.7%

Pr and 48.3% Nd. The sample was adsorbed on the resin from a solution at a pH of 1.8. The flow rate of the eluant was maintained at 1.5 centimeters per minute, and the pH of the citrate was 2.55. The breakthrough came at 184 liters, which, at this slow flow rate, is approximately 2.5 days after the start of the elution.

The total elution curve, with the individual elution curves, is presented in Figure 15. In making the spectrophotometric analyses, the samples were dissolved to give a solution of higher rare earth concentration than the usual 100 milligrams of oxide per 10 millliliters of solution. This was to detect the praseodymium more accurately in the early fractions so that its breakthrough point could be determined. The praseodymium could be observed fairly accurately in amounts as low as 0.5% of the total sample.

The spectrophotometric curves showing the spectra of the original material, an early fraction, and a tail fraction are shown in Figure 16. The neodymium content in the tail fractions could have been reduced still further by carrying out the elution process for an additional period of time.

To show the effect of simultaneous changes in several of the operating conditions, the results of the above experiment are compared with the results obtained in an experiment using a 16 millimeter column, same bed length,

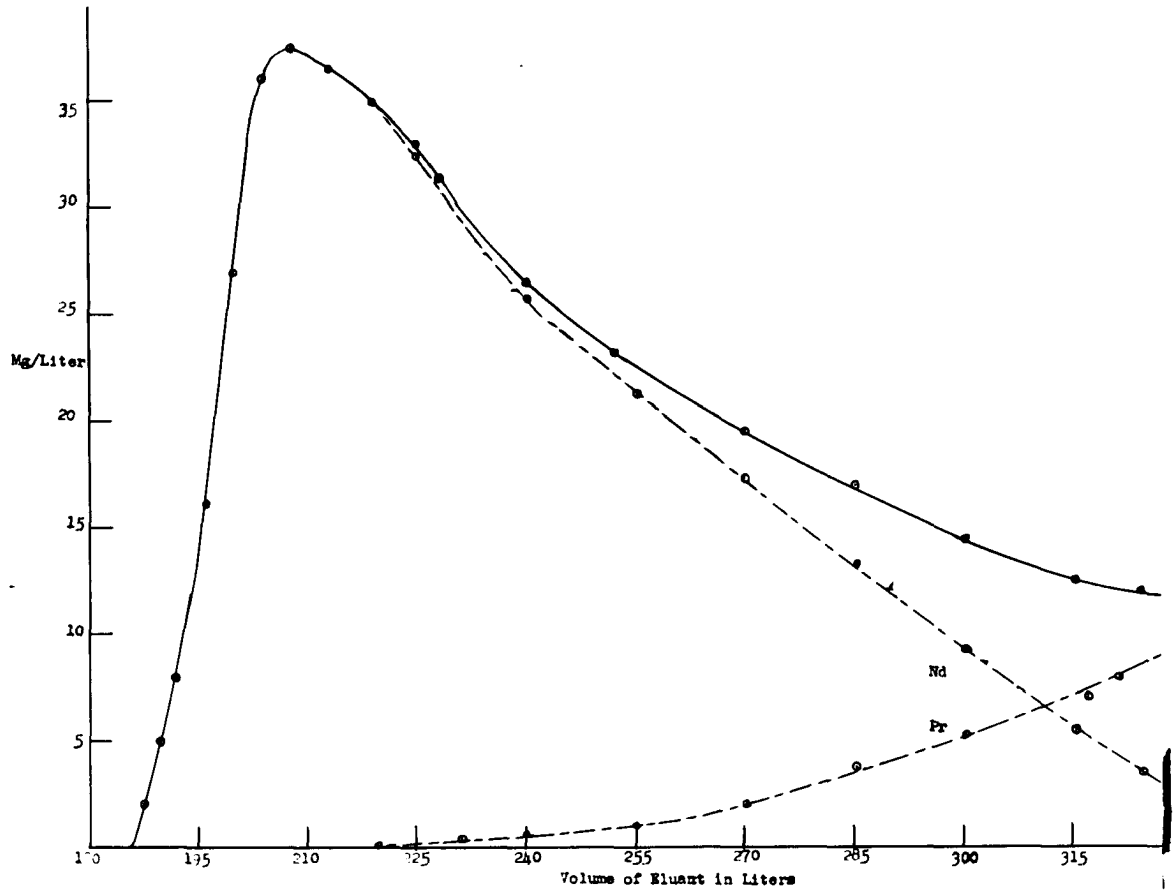

Figure 15. Total elution curve under favorable conditions of operation; column dimensions, 64 mm. x 175 cm.; composition of starting material, 48.3% Nd and 51.7% Pr.

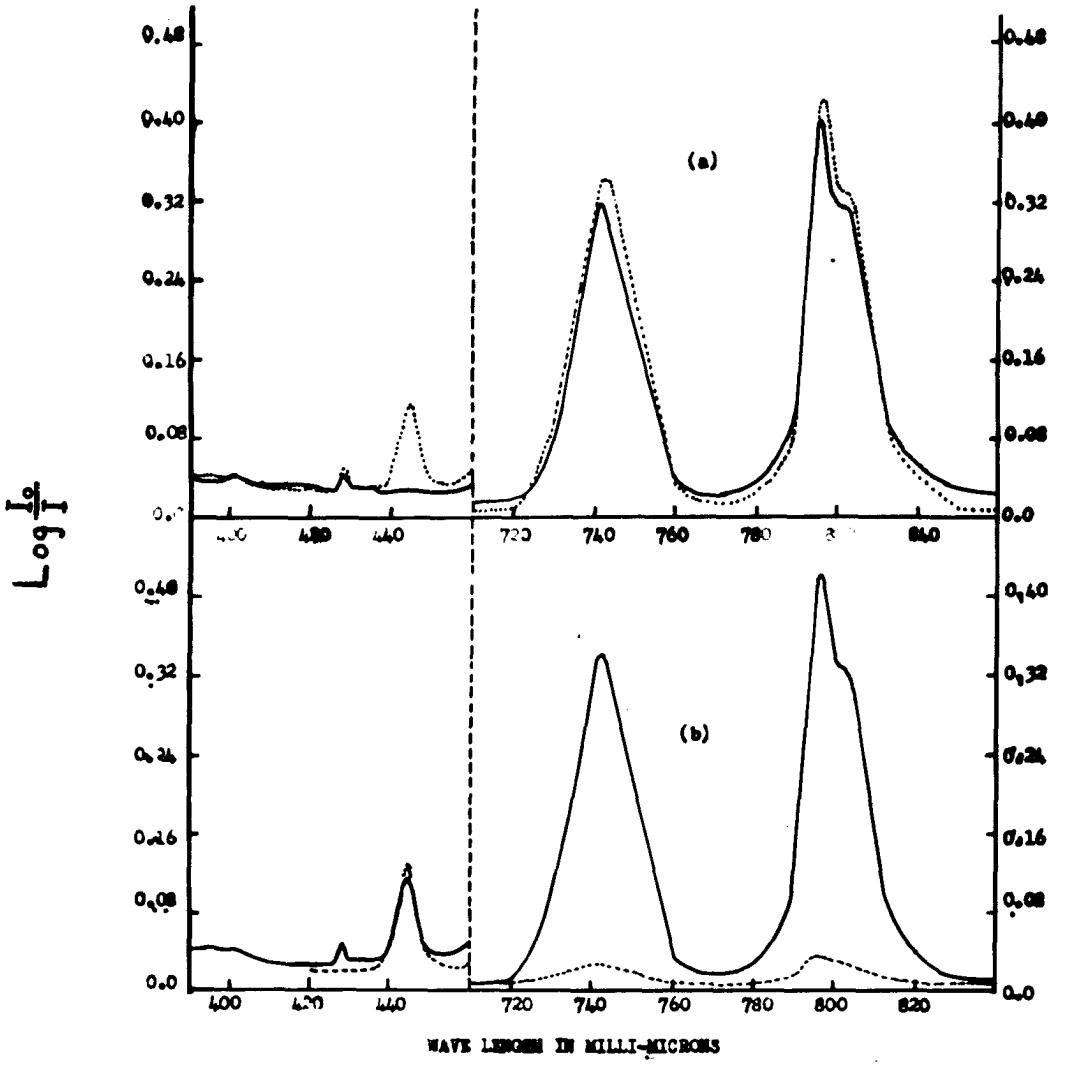

Figure 16. Spectrophotometric curves of samples obtained from an elution under favorable conditions; column dimensions, 64 mm. x 175 cm.; composition of starting material, 48.3% Nd and 51.7% Pr. In (a) the starting sample is shown by the dotted curve, the solid curve being that of a front fraction. In (b), the starting sample is the solid curve with the dotted curve a tail fraction.

the citrate at a pH of 2.55, flow rate of 6 centimeters per minute, and a sample size of 0.5 grams per square centimeter. The only factors which differed appreciably were the diameter, flow rate, and sample size. The material on the smaller column contained 43.4% Pr, compared with 51.7% Pr on the larger column. The small difference in starting composition should favor the separation of neodymium on the 16 millimeter column. The purity curves are presented in Figure 17, showing conclusively that the separation obtained with the column operated under the "standard" conditions represents by far the best separation obtained to date. Approximately 22% of the total neodymium in the starting material was obtained with spectroscopic purity, and 50% with a purity of 98%.

II Separations Performed under Standard Conditions

A true test of the particular set of conditions chosen would be to apply it to numerous mixtures of the other rare earths. A number of minerals containing rare earths were treated chemically to isolate this group of elements and to provide suitable mixtures for the tests. The chemistry employed has been described in detail in part II of the section on experimental procedure. A number of preliminary runs were made which were designed to enrich the fractions. It was found that the binary mixtures of dysprosium -- yttrium, samarium -- gadolinium, and

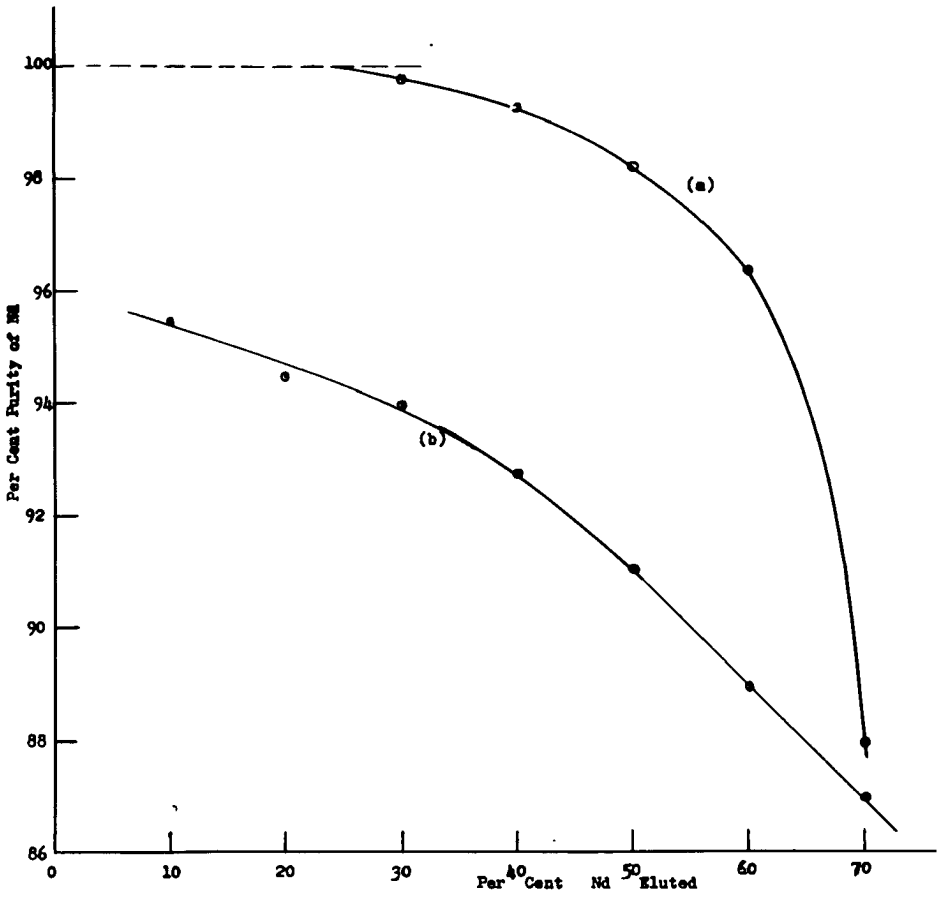

Figure 17. Comparative purity curves between (a) a column operated under favorable conditions and (b) a column operated at an adverse flow rate, sample size, and pH.

holmium-erbium did not separate to any marked extent. Terbium was the one element which presented the most difficulty, as trace amounts or more of this material persist throughout most of the elution. It can be qualitatively detected by the color it imparts to the oxides, only a fraction of one per cent being sufficient to impart a noticeable brown color to the oxide. The ensuing experiments were performed with the difficultly separable mixtures, as well as a neodymium-samarium mixture.

a) Neodymium-Praseodymium. It would be of interest to operate a column under standard conditions using material which initially contains 98% Nd to determine the per cent yield of pure neodymium. The information gleaned from such an experiment should serve as an index as to the maximum overall efficiency of producing pure neodymium from a 50-50 Nd-Pr starting mixture in one or two passes through a column. In a two column process, that material which has a purity of 96-98% Nd from the first column could be readsorbed on the second column and re-eluted to produce a large quantity of pure neodymium.

A total of 1.8 grams of material, containing 98% Nd was divided into two fractions and adsorbed on two 16 millimeter columns, having bed lengths of 175 centimeters. A number of the samples obtained during the course of the elution were given to the spectrographic group for the de-

tection of praseodymium. Since the spectrophotometer cannot detect praseodymium in a sample in amounts less than 0.5%, the spectroscopic method, with a lower limit of 0.1% Pr, is much more sensitive. A total of 1.3 grams of material from the two columns (combined) was obtained which contained less than 0.1% Pr. This represents an approximate yield of 75% of the original neodymium which is produced pure.

The experiment which was described in part I of this section yielded 22.5% of the neodymium pure, while 50% of the neodymium was eluted with a purity of 98%. Hence one can see that in a two column process approximately 40% of the original neodymium in the mixture was obtained pure. It is possible that a larger over-all yield could be obtained by a different choice of the intermediate fraction, i.e., the material chosen for use on the second column. For example, instead of using 98% pure material, a better choice may be 90% or 94% pure neodymium.

If we assume for the moment that the process is to be used with two or more columns, it may also be advantageous to slightly overload the first column with material so that the total amount of enriched material can be increased. However, in the operation of the second column, the standard set of conditions should be adhered to closely.

In the preparation of pure praseodymium, the standard

conditions are utilized; the rich praseodymium coming from the tail end of the elution. In an experiment designed to prepare pure praseodymium, 2.8 grams of oxide containing 98% Pr was eluted from a 32 millimeter diameter column. Analysis of the eluted samples showed that 1.3 grams of material contained less than 0.1% Nd. These results serve to illustrate a point which has been found to be general; in the preparation of pure A and pure B from a mixture AB in which A is eluted first, the efficiency of the process for producing pure A is greater than for producing pure B.

Referring to Figure 15, it can be seen that beyond the peak in the total elution curve the neodymium content in the eluant diminishes gradually. Hence it persists for some time, during which the praseodymium content increases after its breakthrough. Therefore, because of the length of time involved in getting very rich praseodymium samples from a single pass through a column using a 50-50 mixture as the starting material, and also because of the fact that a large portion of the starting material is eluted between the neodymium-rich and praseodymium-rich fractions, the efficiency of the operation is reduced by attempting to produce pure praseodymium in a single step process.

Readsorption as a method of recovering the rare earths from the citrate eluant is practical. It can also

be used as a concentration step to diminish the volume of liquid containing the rare earth material. The pH of the eluate is first lowered to 1.8 by adding HCl. The eluate is then passed through a short column of resin and the rare earths are readsorbed. Desorption can be effected with a relatively small volume of 5% citrate at a pH of 4 to 5.

The readsorption process has several advantages: (1) once the elution curves are determined and shown to be reproducible, all of the eluted rare earths of a desired purity can be collected, (2) the material is removed quantitatively by the readsorption so that the usual losses due to solubility are avoided, (3) subsequent elution can be made by a small volume of eluting solution if desired and (4) further purification by selective elution can be started immediately.

b) Neodymium-samarium. The difference in the basicity between neodymium and samarium is about the same as that between praseodymium and neodymium. For that reason, and the fact that there is a greater difference in the ionic radii of neodymium and samarium than with the neighboring pair, one would expect that the separation would probably be better between neodymium and samarium than between praseodymium and neodymium.

A two gram sample of a 50-50 mixture of neodymium

and samarium was adsorbed on a 32 millimeter column (0.259 grams per square centimeter) and eluted under standard conditions. The total elution curve and the individual elution curves are presented in Figure 18. Approximately 60% of the initial samarium was eluted free from any neodymium.

In the experiment with neodymium and samarium, a spectroscopic analysis of the original mixture revealed only traces of gadolinium and europium. The front fractions of eluted material showed per cent amounts of these elements. The fact that the heavier rare earths were concentrated in the first few fractions provided a stimulus to immediately continue the research using heavy rare earths in the hope that the method of separation is generally applicable to all of the rare earths.

c) Samarium-gadolinium. The starting sample weighed five grams and contained 48% Gd and 52% Sm. A column having a bed length of 175 centimeters and a 32 millimeter diameter was used. The elution curves are shown in Figure 19. The results of the analyses are given in Table 15.

The separation of these elements from each other is very poor. When this same pair of elements was eluted using 0.5% citrate at a pH of 3.8, no separation whatsoever was obtained by Wright and Porter of these laboratories. A large amount of work must still be done to find a good

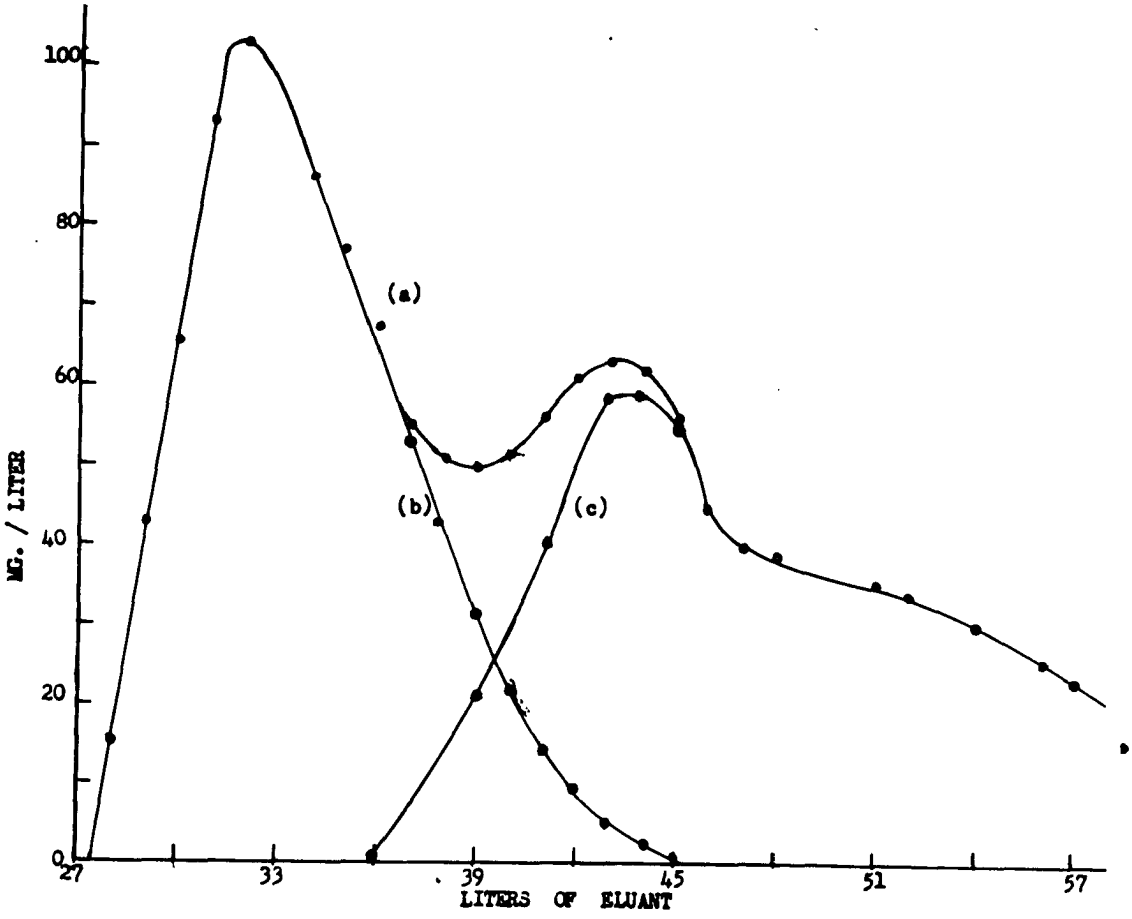

Figure 18. The elution curves of a Nd-Sm mixture: composition of starting material, 50% Nd and 50% Sm; column dimensions, 32 mm. x 175 cm.; weight of sample, 0.259 gr./cm.^{2}, flow rate, 1.5 cm./min. (a) Total elution curve, (b) elution of Nd, and (c) elution of Sm.

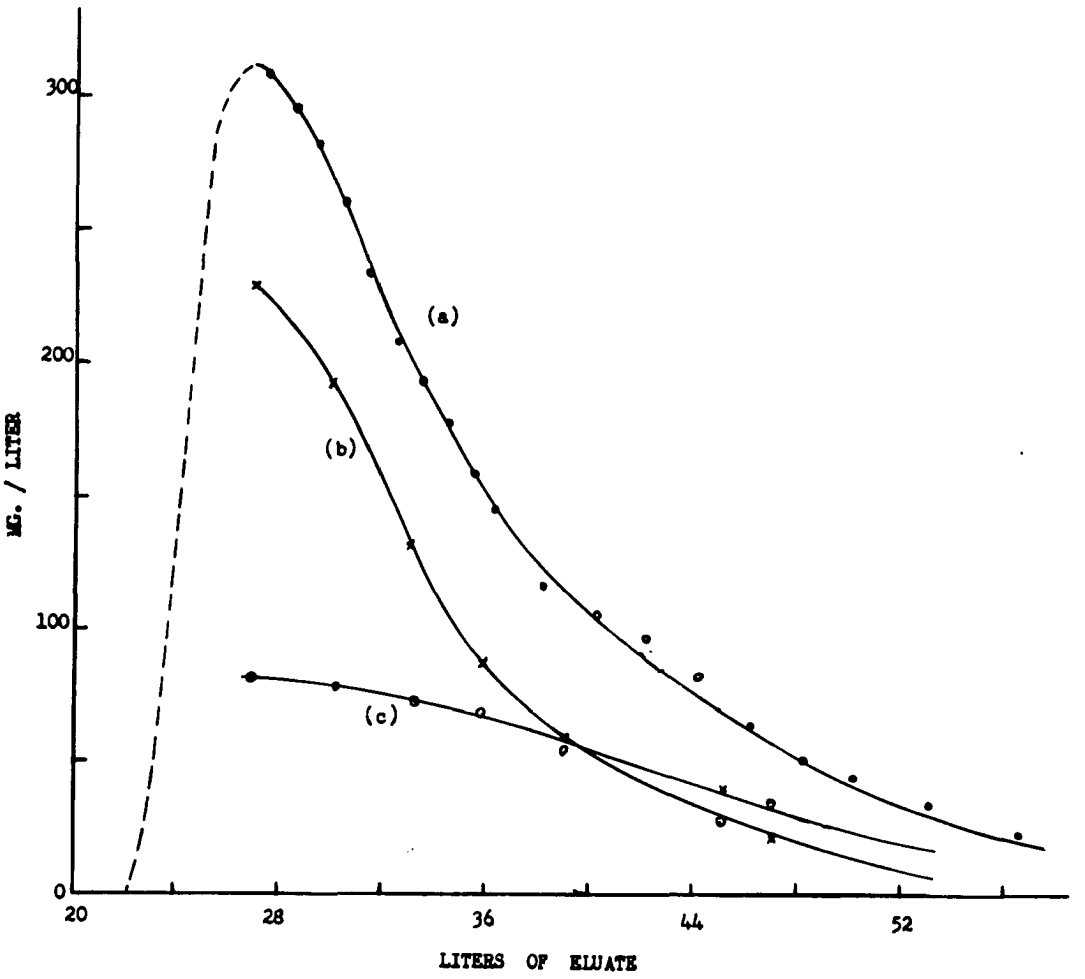

Figure 19. Elution curves of a Sm-Gd mixture under favorable conditions: composition of starting material, 48% Gd and 52% Sm; column dimensions 32 mm. x 175 cm. Curve (a) the total elution curve, (b) the elution of Sm, and (c) the elution of Gd.

method of separating gadolinium from samarium.

TABLE 15

SEPARATION OF Sm FROM Gd

Volume of eluant when sample was taken	% Gd in Eluted Fraction	% Sm in Eluted Fraction
31	50.3	49.7
34	49.2	50.8
38.4	44.6	55.4
44.3	44.1	55.9
50.3	39.4	60.6
62.2	32	68

d) Dysprosium-yttrium. The general chemical behavior of yttrium in any separation scheme places it intermediate to holmium and dysprosium. Any source of material which contains one of the three elements also contains the others. A 32 millimeter diameter column with a bed length of 175 centimeters was used to test the elution of a sample containing 62% Dy and 38% Y.

The breakthrough came with less volume of eluant than was expected, the result being that the nature of the elution curve around the breakthrough point is subject to error. The dotted line portion of the total and individual

elution curves shown in Figure 20 encloses that area which is indicative of the total amount of material in the front fraction, after reclaiming it gravimetrically.

The individual elution curves in Figure 20 were obtained by analyzing the sample on the basis of 200 milligrams of oxide per 10 cubic centimeters and measuring only the 910 mu peak for dysprosium. The yttrium content was obtained by difference, since it has no absorption spectrum. The analytical results so obtained are listed in Table 16.

Here again, as was the case with gadolinium-samarium, the separation is very poor. It is likely that the separation of dysprosium from yttrium could be improved considerably if the elution is carried out at a pH lower than 2.55.

TABLE 16

SEPARATION OF Dy FROM Y

Volume of eluant when sample was taken	% Dy	% Y
27.5	73.5	26.5
30.5	71.0	29
33.5	65.5	34.5
36.3	58	42
40.1	55	45
46.1	52.3	47.7
48.1	38.5	61.5

e) Erbium-lutecium. The prebreakthrough material from a

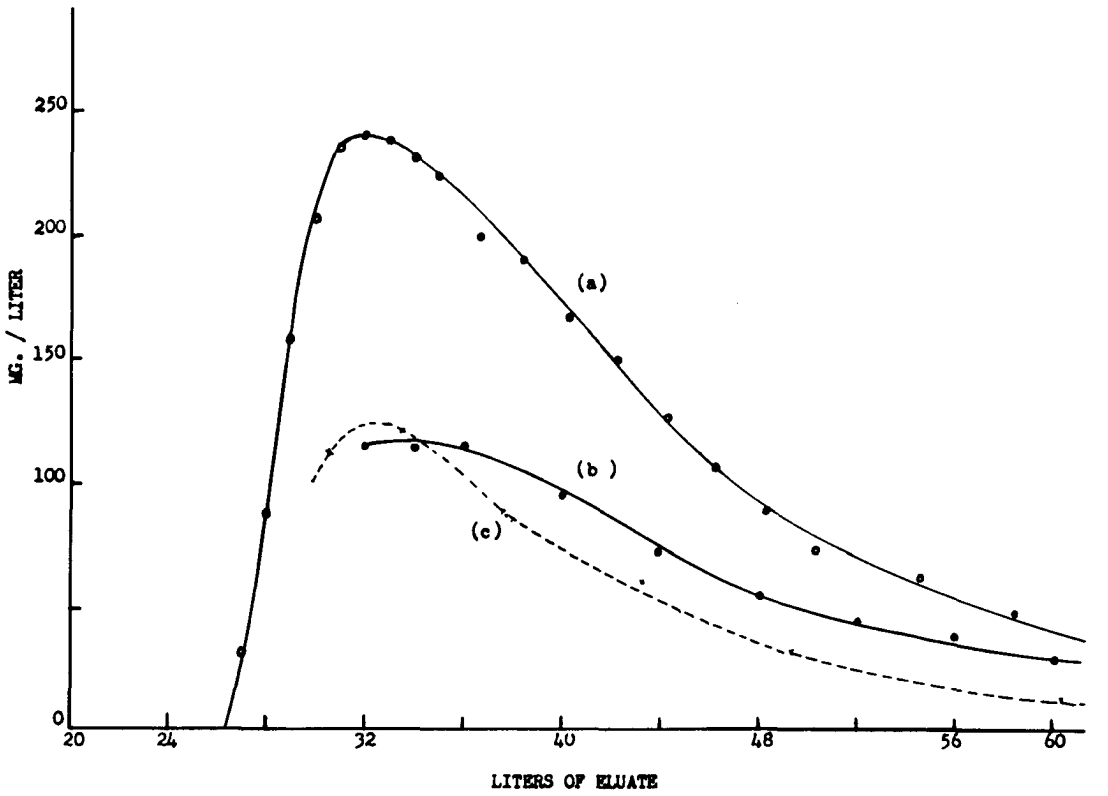

Figure 20. Elution of a Dy-Y mixture under favorable conditions: composition of starting material, 62% Dy and 38% Y; dimension of column, 32 mm. x 175 cm. Curve (a) the total elution curve, (b) the elution curve of Dy, and (c) the elution curve of Y.

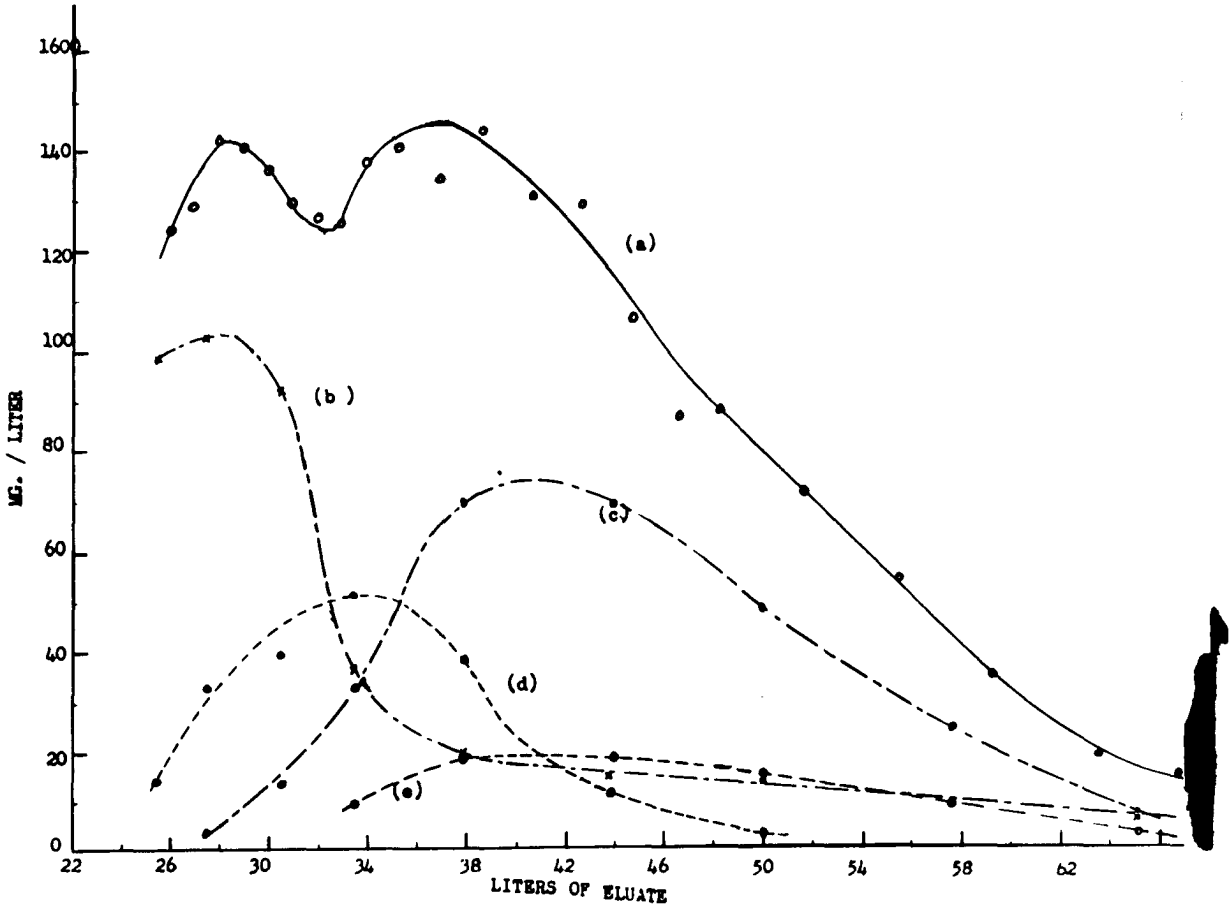

Figure 21. Elution of a heavy rare earth mixture containing principally lutecium and erbium under favorable conditions. Column dimensions, 32 mm. x 175 cm. Curve (a) the total elution curve, (b) elution of lutecium plus other non-detectables, (c) elution of erbium, (d) thulium, and (e) holmium.

large column run using the total heavy rare earth mixture from gadolinite was extracted with 0.5% Na-amalgam to remove the ytterbium. A five gram sample of the material remaining after the extraction was adsorbed on a 32 millimeter column and eluted under standard conditions. Using the extinction coefficients as listed earlier, the analysis of a 200 milligram sample of the starting material showed 33.2% Er, 16.8% Tm, 11.3% Ho, and 38.7% undetectable. The undetectable material, obtained by difference, includes lutecium, with some ytterbium and possibly scandium. The principal components in the mixture are erbium and lutecium.

Because of the high solubility of the oxalates of ytterbium and lutecium in 5% citrate solution, the breakthrough was not detected at low rare earth concentrations in the course of the elution. The pre-breakthrough material was therefore readsorbed and recovered.

The two peaks in the total elution curve show that with the small amount of ytterbium in the original mixture the lutecium and erbium elution peaks are actually fairly well removed from each other. The total elution curve, along with the individual elution curves of each of the constituents are shown in Figure 21. The data from which the curves are drawn are given in Table 17. An examination of the figure shows that the valley between the two elution peaks is much higher than would actually have been the case if thulium had been absent from the starting

material.

The apparent straggling in the elution of the undetectable fraction is probably due to a small amount of yttrium or scandium in the original sample which became concentrated in the tail fractions of the elution. The presence of holmium throughout such a large volume is unexpected.

It can be concluded that lutecium and erbium can be separated conveniently from each other in one or two passes through a column.

TABLE 17

SEPARATION OF THE HEAVY RARE EARTHS
UNDER STANDARD CONDITIONS

Vol. of eluant when sample was taken	% Lu, Yb and other undetectables	Per Cent Eluted		
		Tm	Er	Ho
26	87.5	12.5	--	--
28	73.8	23.4	2.8	--
31	68.7	29.4	9.8	--
34	28.3	39.8	24.8	7.1
38.7	13.6	26.0	47.8	12.6
44.7	13.4	9.9	60.3	16.4
51.6	16.9	3.5	60.7	18.9
59.3	22.8	--	56.2	21.0
68.8	35.4	--	42.3	22.3

DISCUSSION

I Experimental Difficulties in the Separation Process

As in any method for the production of a material there are a number of unforeseen difficulties that arise which must be overcome in the course of developing the process. In the process at hand, a number of experimental difficulties arose which either had to be corrected or else neglected after closely examining their effects upon the separation.

a) Mold growth. It is a well known fact that a citric acid medium is very favorable to the growth of a number of varieties of mold spores. The growth of molds in the citrate solutions used in the experiments previously described has been a troublesome factor in attempting to get reproducible results. The mold problem was particularly acute in those columns which were erected in rooms which had been previously used for microbiological studies.

Fulmer and Werkman (59) list the following acids as being produced by mold action on citric acid: acetonedicarboxylic acid, glycollic acid, glyoxylic acid, malonic acid, and oxalic acid. The one acid most commonly formed is oxalic. This is serious, as insoluble rare earth oxalates would form in the resin bed and not be eluted. The molds also reduce the pH of the eluant and conceivably

block the pores and surfaces of the resin.

Since an elution under the standard set of conditions adopted in this research requires at least several days to perform, a mold has sufficient time to grow in the citric acid solution. While the eluant was filtered before admitting it to the resin column, some spores would get through and become adsorbed within the resin bed. Once there, the mold can not be removed from the resin by ordinary chemical means. Treatment with strong hydrochloric acid was ineffective, either in preventing the growth of the mold, or in removing it. The mold only became dormant, and resumed its growth when the conditions for growth became favorable again. The action of the mold is to grow and encompass the resin particle, rendering it useless as an ion exchange medium. As a result, the shapes of the elution curves change and the breakthrough volume of eluant decreases with each successive experiment conducted under similar conditions.

In the first efforts to solve this problem, toluene was used to prevent mold growth. This reagent was not satisfactory as it introduced a second liquid phase to the eluant. The most desirable control chemical should be effective in low concentrations, economical, easy to handle under control conditions, and not interfere with the reproducibility of the elution curves after prolonged use.

Dr. Fulmer suggested that phenol would meet the requirements and subsequent experiments were performed by Messrs. J. M. Wright and P. Porter.

Spore cultures of Aspergillus oryzae and of Aspergillus niger were used for massive spore inoculation of 0.5% citric acid solution adjusted to pH 4.0 with ammonium hydroxide. The phenol concentrations varied over the range from zero to 1.0 grams per 100 millliliters of citrate solution. After six days, a slight trace of growth was noticed in the solution containing 0.05 per cent phenol but no growth in the higher concentrations. It was decided to use 0.1 per cent phenol in the citrate eluant, thereby giving a safety factor of about two. When actual elution experiments were conducted using didymium and 0.1% phenol in the citrate solution it was found that the elution curves were identical with each other. During an ensuing period of five months in which the phenol treated citrate solution was used with the same columns of resin, no growth of mold has been observed.

The discovery and use of phenol as a mold growth inhibitor has proved itself of great importance in making the ion-exchange process practical for producing pure rare earths.

b) Inconsistencies in maintaining the flow rate. Proper control of the flow rate has a very decided effect upon the separation. In the particular set of standard

conditions which has been proposed, the actual flow rate in milliliters per minute becomes very low when small diameter columns are used. The means of regulating the flow rate on the columns in this laboratory have been with a stop cock or a screw clamp arrangement on a rubber hose connection. Neither one is too satisfactory. Then, too, one must consider that a certain amount of packing takes place within a resin bed during the course of an experiment, which materially lowers the flow rate. The flow rate will also change when the amount of solution head above the resin bed changes. The level of the liquid in the column above the resin bed must be checked periodically to be sure that the columns are not running dry. If the column should go dry, the experiment is ruined and must be repeated. The experimenter must also check the flow rate at frequent intervals to see that it is of the proper constant value.

II An Interpretation of the Mechanism of the Separation

From the experimental evidence which has been presented, it becomes necessary to consider the chemical reactions which take place during an experiment. Let us assume that we are working with only one rare earth element, and not a mixture.

With the resin in the hydrogen cycle, addition of the solution of rare earth ions causes an exchange.

$$M^{+3} + 3\,HR \rightleftharpoons 3H^{+} + MR_3 \qquad (10)$$

M^{+3} represents the rare earth ion, HR the acid form of the resin, and MR_3 the rare earth form of the resin. At a pH of ~2.0, the equilibrium is overwhelmingly shifted to the right, which accounts for the ability of tracer quantities ($\sim 10^{-10}$M) of rare earths to be adsorbed at the top of the resin bed.

Addition of the citrate solution with the labile NH_4^+ ions causes a conversion of the remainder of the resin bed to the NH_4^+ form. This is evidenced by the "conditioning lag," during which time the effluent citrate has a pH of 1.8, which is the pH of a 5% citric acid solution. During this time the H^+ ions are being replaced by NH_4^+ ions, resulting in the ammonium cycle of the resin. The reactions between the rare earth, citrate, and ammonium ions which can now take place are postulated as:

$$nMR_3 + 3nNH_4^+ \rightleftharpoons 3nNH_4R + nM^{+3} \qquad (11)$$

$$nM^{+3} + 3(HyCit)^{y-3} \rightleftharpoons M_n(Hy\ Cit)_3^{y-3} \qquad (12)$$

$$M_n(H_yCit)_3^{y-3} + 3nNH_4R \rightleftharpoons nMR_3 + 3nNH_4^+ + 3(H_y\ Cit)^{y-3} \qquad (13)$$

M^{+3} is the uncomplexed rare earth ion, $(H_y\ Cit)^{y-3}$ is some citrate ion, the exact composition of which is unknown, and n is restricted by the equality n = 3-y. Reaction (11) is the initial desorption, or ion-exchange step, which serves the purpose of placing the rare earth ion into solution. Once in solution, the ion can undergo further reactions

such as the complexing reaction (12), or it can react in the reverse direction of (13). Equation (13) shows the possibility of the complex reacting directly with the ammonium resin, which again produces MR_3. By adding equations (12) and (13), one can obtain (11). It has been stated earlier that the exact composition of the complex is not known. It is doubtful if the complex actually exists as written in equation (12), but it may be a Werner type complex. This could be one means of controlling the M^{+3} ion concentration in the solution.

During the course of the elution, reactions (11) (12) and (13) are assumed to be either at equilibrium or close to it. Movement of the rare earth down the column results from the direction of the natural flow of eluant. New and available exchange points on the resin at a slightly lower position in the column are presented for the rare earth ions to use, provided that the new exchange points are in that proper form which undergoes exchange. The flow rate will determine to some extent the relative number of adsorption-desorption cycles which any one rare earth ion makes while in the column, other operating conditions remaining constant.

A conclusive answer to the question of the great dependence of the separation upon the pH of the citrate can not be given at this time. However, a few pertinent facts can be given which may shed some light upon the

subject. In a 5% solution of citric acid, the concentration of the $(H_2Cit)^-$ ion reaches a maximum value at pH 3.2. At a pH of ~2.0, the concentration of this particular ion is practically zero. The curve showing per cent of ion type as a function of the pH of the solution for a given ionic strength can be calculated from the dissociation constants of citric acid. The concentration of the $(H_2Cit)^-$ ion is ~25% of its maximum value (for a 5% solution) when the pH is 2.55. It has been shown by Tompkins and Mayer (50) that the $(H_2Cit)^-$ ion is the one which plays the leading role in the separation process. It would not be safe to conclude that the separation is effected by the concentration of the $(H_2Cit)^-$ ion in the solution. Instead, it would be more logical to consider that (1) the difference in the stabilities of the complexes increases as the pH is decreased, (2) the concentration of the $(H_2Cit)^-$ ion (which is necessary to form the complex) increases with the pH in this region with the result (3) that the separation reaches an optimum value in the pH range of 2.55 when 5% citrate is used as the eluant.

Straggling of the material on the resin, so that an ever increasing band width is produced, results from operating the column at too high a flow rate. Consider the resin particle to consist of a lattice, with accessible exchange points within, as well as on the surface of the

particle. A rare earth ion will exchange at the first available NH_4R exchange point, which would generally be at or near the surface of the resin particle. Those exchange points which are deep inside the resin are reached by the rare earth only after diffusing into the lattice of the particle. An adsorption-desorption cycle in which the rare earth ion starts and ends in the great body of solution surrounding the resin particle takes more time when exchange takes place within the resin than at the surface. Then, too, the number of times the rare earth ion exchanges within any one resin particle before it emerges again is considerably greater with that which diffuses into the resin. The net result is that those rare earth ions which exchange near the surface are eluted from the column much faster than are those which penetrate the resin particle. Under equilibrium conditions of operation of the column there would be no great difference in the number of exchanges which the ions make so the actual elution curve should approach the theoretical elution curve. The theoretical curve is that proposed by the Wilson theory referred to earlier in this thesis.

When a mixture of rare earths is employed, the same process and set of reactions (as reactions (11) (12) and (13) above) holds for one rare earth species as for any other. Any separation will depend upon the relative stability of the citrate complex of one rare earth to the

others. Inasmuch as many column volumes of eluant must be passed through the resin bed before the breakthrough, under the controlled pH conditions, the rare earths spend most of their time as MR_3. Due to differences in the basicities of the rare earths (53), the stability of the rare earth citrate complexes will differ. Those that are more stable (under the constant and controlled pH) will stay in solution a longer time before exchanging with the NH_4^+ on the resin. During this time the more stable complex is moved down the column a greater distance (on the average) than are the other rare earth complexes. Coupled with the notion of separation through differences in complex stabilities, is the relative strengths of the bonds connecting the rare earth ions to the resin. It is believed that these are different for each rare earth, as will be shown in the next section.

The difference between the stabilities of the complexes of each neighboring pair of rare earths is very small. The difference seems to decrease with increase in atomic number. Hence the efficiency of a separation will depend upon the average number of exchanges which one rare earth ion species makes in relation to that of the other rare earths during the total course of the elution. As one can readily see, this is favored by a slow flow rate and a long column.

The elution of macro quantities of rare earths differ in one respect from a similar elution using tracer amounts. The number of rare earth ions present in an experiment using tracer amounts, in relation to the total number of exchange points on the resin, permits the free and independent elution of each of the ion species in the mixture. Each ion behaves independently, as if it alone were on the column. Such is not the case with macro amounts of material. A definite competition is established between the various rare earth complexes for the exchange points on the resin. That rare earth whose citrate complex is most stable will stay in solution longest, as the exchange points are preferentially held more tightly by the other rare earths. The net result is that the separation is enhanced as is evidenced by the following observations: (1) the elution of macro amounts of cerium and yttrium gave better separations than tracer amounts under the same conditions, (2) the existence of an optimum weight of sample, and (3) the breakthrough occurs with a smaller amount of eluant. The lack of competition of the ions for the exchange points in the case with tracer amounts can, in part, account for the insistence of the group at Oak Ridge (Boyd, Tompkins, et al) of using a pH 2.85 citrate solution for eluting rare earth fission products.

III Intercorrelations of the Experimental Results with Notions of Ion Size and Basicity

If a sample were prepared that contained equal amounts of each of the rare earths and yttrium, adsorbed on an Amberlite IR-1 column, and eluted with 5% citrate, the order in which they would emerge from the column would be Lu, Yb, Tm, Er, Ho, Y, Dy, Tb, Gd, Eu, Sm, 61, Nd, Pr, Ce, and La. With the exception of yttrium, this is the same order as the decrease in atomic numbers.

The forces which bind atoms together in a molecule are, for the most part, coulombic in nature. Applied to the case of a resin anion and a cation in solution, the electrostatic attraction can be expressed by the relation

$$F = \frac{e_a e_c}{(r_{ac})^2} \qquad (14)$$

where F represents the force of attraction, e_a the charge on the resin anion, e_c the charge on the cation, and r_{ac} the equilibrium distance of the cation from the anion. The numerator shows that the multivalent cations are held more tightly than are cations of a lower valence type. The denominator states that with ions of the same type, the electrostatic force of attraction is inversely proportional to the square of the ionic radii.

In the case with crystals, the ionic radii of the ions in the same family and group in the periodic chart increase with increasing atomic number. However, an ion

in aqueous solution becomes hydrated, due to strong ion-dipole attraction. The net result is that the order becomes reversed. For instance, in Group I-A of the periodic chart, the order of increasing ion size is Cs, Rb, K, Na, Li and H. The number of water dipoles that form the sphere of hydration around the cation depends upon the polarizing ability of the cation. The ability of an ion to induce attraction with a dipole has been found to increase with the charge on the ion and to decrease with the crystal ionic radius (54). Applying this line of reasoning to the rare earths one can see that the ionic radii of the hydrated ions should increase as the atomic number is increased. The force of electrostatic attraction between the hydrated rare earth cation and the resin anion decreases with an increase in atomic number since r_{ac} increases. The position of yttrium in the elution scheme corresponds to the position of its hydrated ionic radius, which is intermediate to dysprosium and holmium.

The basicities of the trivalent rare earths show that the decrease in pH at which precipitation of the hydroxide occurs follows the direction of increasing atomic number and parallels the decrease in the ionic radius. Placing the experimental results of the basicities on a relative basis with yttrium = 1, Moeller and Kremers (55) obtained: La, 1235; Ce, 185; Pr, 33.3; Nd, 23.5; Sm, 8.4; Eu, 4.2; Gd, 2.6; Er, 0.16; Tm, 0.041; Yb, 0.036; and Lu, 0.031. If basicities were the dominant factor in effecting a separation

of the rare earths on the column, one of the very difficult separations would be between thulium, ytterbium, and lutecium.

The order of basicities as applied to the order of elution show that the least basic rare earths are eluted first. This can be regarded in the same sense as a stronger base replacing a weaker one on the absorbent (56).

SUMMARY AND CONCLUSIONS

The research which has been described in this thesis was designed to obtain a set of conditions for the mutual separation of the rare earths in high yield and in a relatively short time. It has been shown that the method of ion-exchange under controlled conditions of elution can be applied to the production of relatively large amounts of rare earths of spectroscopic purity. The time necessary for the complete operation is a matter of a few days, in comparison with the old method of fractional crystallization which required months.

Not all of the factors that could influence the separation have been investigated. Among these are temperature, the choice of eluant, and the choice of the ion-exchanger. The change to another resin would almost certainly result in a necessary change in the pH of the citrate and the flow rate, since different functional groups may be present in the resin. Also, the capacity of the resin and the rate of attaining equilibrium may not be the same as for Amberlite IR-1. Any other factors that remain uninvestigated are probably of minor importance and would have no great effect on the net results.

The effect of citrate concentration on the separation is of major importance, and in the course of this work it was not investigated fully. It was shown that with each

concentration of citrate there corresponds a pH range which can be used for separating the rare earths. It is very likely that a better citrate concentration and pH value exist than those which were adopted in this work. The present use of 5% citrate was purely arbitrary.

In the separation of macro quantities of rare earths, the 5% citrate used as eluant is much more effective as the pH is lowered, the optimum value being ~2.55. At pH values below this, larger amounts of eluant and much more time is required for the elution without any pronounced increase in the separation. The value of 2.55 ± 0.02 pH units represents a true optimum value.

If the starting material is highly enriched in one rare earth species, then a considerable yield of pure rare earth can be obtained. Thus a series of columns can be used to further purify the rich fractions, leading to a pure product in two or three passes through the column. This can be expedited by readsorbing the effluent containing the enriched fraction on another column after adjusting the pH of the effluent to 1.8.

The process of readsorption on another batch of resin serves as a means of concentrating the eluted material. In the case of the heavy rare earths, viz. lutecium, thulium, and ytterbium, the solubilities of the oxalates in citric acid solution is quite high, so that a large percentage of

them is lost through solubility unless they are concentrated in a smaller volume. As the heavy rare earths are the first to be eluted, the entire effluent, from the start of the desorption to the observation of a noticeable amount of oxalate precipitate, is readsorbed. Many grams of valuable rare earths have been retained as a result of this step.

The experiments on the effect of column length have shown that the concentration peaks of the components on the resin move farther apart as the column length is increased. However, beyond a certain length of column the separation does not seem to increase since the bands spread out and straggling and overlapping of the bands result.

Straggling is intensified when small starting samples are used, as was shown in the experiment with a 600 centimeter column using cerium and yttrium. The effect of straggling is also illustrated in the data in Tables 9 and 11 which show the effect of sample size on the breakthrough volume and the degree of separation. A comparison of the breakthrough points with corrected bed lengths shows that straggling and possibly free diffusion occur in the column to a greater relative extent with smaller samples. Below a certain optimum range of sample weights, the separation is lessened. Conversely, the use of too large a sample also decreases the separation. Two effects are probably important in regard to the latter: (1) the fraction of the

column occupied by the sample in the initial adsorption step, and (2) the width of the band as it proceeds down the column.

The possibility that the straggling and overlapping of the bands in the column arises from operating the column under conditions too far removed from equilibrium seems very real in the light of the evidence reported by Tompkins and Mayer (57), and Powell and Butler (58). Since these investigators used operating conditions which were not entirely the same as those used in the present work, additional experiments will have to be performed at much slower flow rates to allow sufficient time for the diffusion of the ions to take place into, and out of, the resin.

The choice of the length of the column is largely arbitrary. Increasing the length of the column and decreasing the flow rate and pH of the eluant produce a greater separation, but at the expense of the amount of time necessary for the elution. The time factor increases enormously as the pH and flow rate are changed in the above directions, and becomes a determining factor in any large scale operation. Choices have to be made, as pertains to the column length, which depend upon the object of the particular experiment to be undertaken.

Since the diameter of the column can be increased without affecting the separation adversely, larger amounts

of material can be processed. With larger columns, the need of a thorough, initial backwashing becomes paramount in importance, otherwise channelling will result which in turn reduces the yield of pure product. An experiment on a large diameter column can be made in the same length of time as an experiment conducted under the same conditions with a small diameter column. Thus, the process lends itself to operation on a scale which is considerably larger than the scale used in the experiments described in the body of this thesis. At the present time, a number of columns having diameters of four inches are being used which are each capable of processing 125 grams of material per column in each elution.

It is not intended that the set of conditions which were adopted as standard should be interpreted as producing the highest possible yield of pure product. Since the ammonium ion, rare earth ion, and citrate ion concentrations are intimately inter-related, any number of sets of "optimum" conditions can be chosen. It is very likely that in the near future a theory will be advanced which will describe the ion-exchange process more completely, and may even propose the use of a variety of operating conditions for any degree of separation.

In conclusion, the author is of the confirmed opinion that the ion-exchange method for separating the rare earths

from each other is by far the best general method known at the present time. Improvements in technique and alterations in some of the operating conditions should produce greater yields of pure compounds.

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